JOURNAL OF

July 1955

CHEMICAL EDUCATION

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Atom Model Sets for Elementary Organic Chemistry

With only nine different types of atom models, it is possible to construct true-to-scale molecular models of most compounds discussed in a first-year organic chemistry course. Stuart and Briegleb atom models, manufactured in Western Germany by E. Leybold's Nachfolger and distributed in North America by Arthur S. LaPine & Company, give an exact picture of the actual spatial arrangement of a chemical compound. The models are spheres or ovoids with cut surfaces which can be joined together by means of quick fasteners. Lateral surfaces are arranged in such a manner that internuclear distances and effective radii of constructed molecules are reproduced in an enlargement of 1.5 x 10^8 with the correct valence angles and spatial arrangement. Carbon models, for example, have various shapes with differently arranged lateral surfaces depending upon the type of bond.

Models for Double Bonds

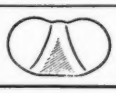
The models for carbon in ethylenic double bonds and in aromatic compounds; for oxygen in carbonyl groups; and for the nitro group are not spherical but prismatic in shape. Thus, according to Briegleb, the unsymmetrical nature of the charge distribution of π-electrons, which are responsible for the double bonds, is reproduced. The ellipse-shaped sections of such double bonds indicate that a stable equilibrium exists, and that any displacement of the substituents out of their plane requires considerable expenditure of energy.

On the other hand, with respect to the directions of the single bonds (σ-bonds), the substituents can rotate freely because of their rotation symmetry, and can be hindered only by their spatial arrangement. In order to prevent them from rotating, the elliptical surfaces of the models for double bonds each has two slots into which spring metal wedges are pressed.

Constructing Molecular Models

Hydrogen and chlorine models are fitted with permanent quick fasteners. Other models are joined by means of quick snap-on fasteners. Spring metal wedges should be pressed into the slots of models used in double bonds to prevent rotation.

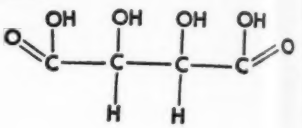
In the next column are shown the nine types of atom models required for elementary organic chemistry demonstrations.

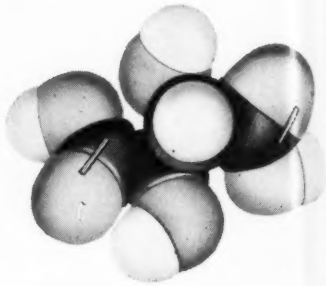
Symbol	*View*	*Number Required*
H—		14
Cl—		3
C		6
C		4
C		6
N		2
O=		2
O		6
N		1

The following are examples of molecules that can be constructed from these nine types:

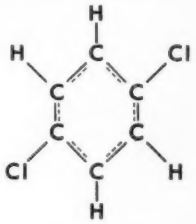
2,3-dimethyl-butane	methyl-propene
butadiene	2-chloro-propane
tertiary isobutyl alcohol	diethyl ether
ethylamine	hydrazine
hydroxylamine	nitromethane
acetaldehyde	acetone
isobutyric acid	acrylic acid
ethyl acetate	acetic anhydride
formamide	phosgene
urea	glycol
glycolaldehyde	lactic acid
adipic acid	maleic acid
alanine	citric acid
hexose	glucose
nitro-benzene	acetanilide
benzophenone	cinnamic acid
cyclohexane	coumaric acid

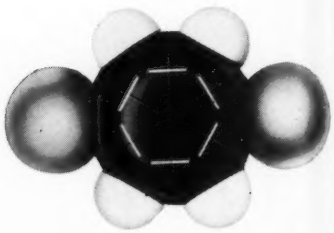
Tartaric Acid (2 optically active C-atoms)





Paradichlorbenzene





Applications

Stuart and Briegleb molecular models are invaluable aids in demonstrating many of the aspects of geometrical and optical isomerism, tautomerism, resonance, three-dimensional arrangements of macro-molecules, various types of steric effects, biochemical specificity, and other chemical phenomena.

Available upon request is a booklet describing the School Set of Atom Models in further detail and listing many more molecules that can be constructed from these models.

Catalog No. CE302-82, School Set of 44 Pieces of 9 Types of Atom Models, distributed as in table, complete with 24 Quick Fasteners, 1 Ejector Tool, and 24 Spring Metal Wedges, each 43.50

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July, 1955

NUMBER 7

JOURNAL OF CHEMICAL EDUCATION

A Notation for the Study of Certain Stereochemical Problems, *Melvin S. Newman* 344

The Royal Cork Institution, *Margaret MacSweeney and Joseph Reilly* 348

A Setup for Two-dimensional Paper Chromatography, *E. C. Mathew and B. M. Das* 352

Distance Factors in Paper Chromatography, *Conrad William Batt, F.S.C., and George N. Kowkabany* 353

Location of the Decimal Point in Slide-rule Calculations, *Helen G. Husted* 354

Chemical Furnaces of Ancient Mesopotamia and Palestine, *Martin Levey* 356

Inserting Bulbs in the Victor Meyer Apparatus, *Jeremiah J. Iannucci and Norbert Isenberg* 359

The Examinations Program of the Division of Chemical Education, *Theo. A. Ashford* 360

A Mnemonic for Dicarboxylic Acids, *Gerald J. Cox* 363

Simple Apparatus for Refrigeration Experiments, *M. A. Govinda Rau and M. G. Subba Rau* 364

Synthesis of Copper (I) Sulfide, *Samuel R. Scholes, Jr.* 365

The van der Waals Gas Equation, *Ellice S. Swinbourne* 366

How to Use Radiocarbon Chemicals in Teaching, *Richard H. Robinson* 370

Berzelius' *Jahresbericht* and the International Organization of Chemists, *Wilhelm Ostwald* 373

Automatic Safety Trap for Laboratory Steam Distillations, *Edward M. Hubbard* 376

Colligative Properties, *Francis P. Chinard* 377

Separation and Detection of the Aluminum Ion in Qualitative Analysis, *Sterling B. Smith and John M. Shute* 380

Modified Ramsey-Young Apparatus for Measuring Vapor Pressures of Liquids, *Walter H. Dumke* 383

The Line Integral in Chemical Thermodynamics, *Robert M. Kallo* 384

Report of the New England Association of Chemistry Teachers Official Business 386

Editor's Outlook 343

Out of the Editor's Basket 19

Recent Books 388

Frontispiece—Portable Oven from Third Millenium B.C. 15

Advertisers' Index 30

Tested Demonstrations in General Chemistry 11, 12

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Haze measurement..a valuable analytical tool

Photo-Nephelometry measures haze and turbidity in liquids, at extremely low concentrations

Clarity of Whiskey, Beer, and Other Beverages

One of the most widespread and effective applications of Coleman Photo-Nephelometry is the measurement of haze in whiskies, wines and other beverages. Evaluation of filters and filter media and the control of haze in bottled whiskies is now a standard procedure throughout the distilling industry. Nephelometry precisely predicts the final clarity of the finished product.

Sterility of Biologicals

The measurement and control of clarity and sterility of parenterals such as Penicillin, Streptomycin, Dihydrostreptomycin, Neomycin Sulfate, and Vitamin Solutions is an important use of Nephelometry.

Precipitates in Industrial Waters

Purity and suitability of industrial waters and other liquids is easily evaluated with the Nephelometer, especially at very low concentrations. For example: Electric generating plants now use Coleman Nephelometers for the evaluation and control of feed waters for high pressure boilers. Control is accomplished by Nephelometric measurement of calcium (Range 0.0-0.5 PPM) in the feed water.

Bacteriological Growth Rates and Effects of Nutrients and Inhibitors

In bacteriology the study of the effects of nutrients and inhibitors on growth rates of bacteria has been given new impetus and significance by the simplicity and precision of the Nephelometric method. These studies include a wide variety of bacterial types, including: Leptospira, Actinomyces Bovis, Tubercle Bacilli, Esch. Coli, Staphylococci.

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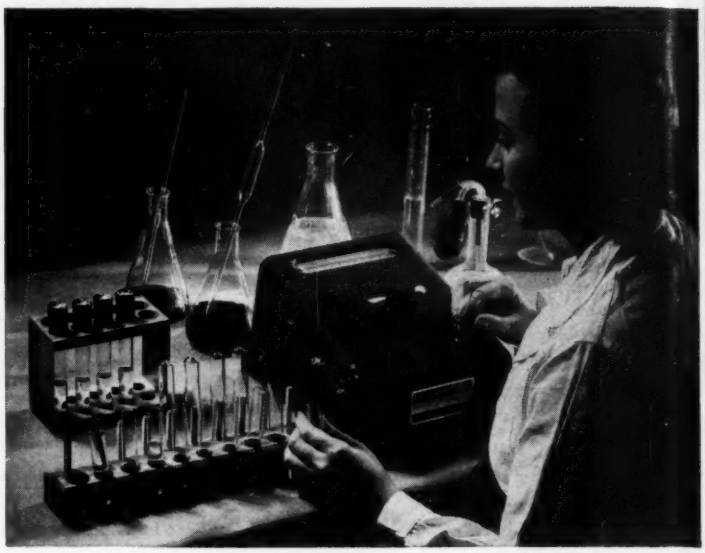
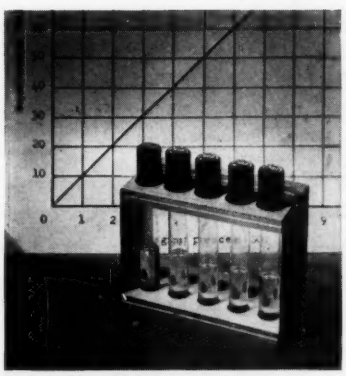
A Precise Notation for Haze

The Coleman Nephelos Standards used with a Coleman Nephelometer provide an accurate numerical notation system. Haze data can be expressed on a fixed, numerical scale to set standards or reproduce procedures.



Operation is simple. Routine work can easily be handled by people with limited training.



Coleman Certified NephelosStandards express entire haze range on a continuous numerical scale.

Two models. Coleman Nephelometer (Model 7) for Nephelometry, and Coleman Nepho-Colorimeter (Model 9) for Nephelometry and Colorimetry. Ask for Bulletins B-213 and B-215.

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7. ENERGY

A. HEAT ENERGY

Exothermic reactions

7-1 Match, wooden tongue depressor, lump coal, paper. **Burn. Show energy off.**

*7-2 See Figure 7-2. Conc. H_2SO_4, 250 ml. beaker, ether, 6mm tubing 30 cms. long with 0.5 ml. bulb blown at closed end. Fill bulb with ether, and place in 50 ml. conc. H_2SO_4. **Suddenly dump 50 ml. water upon the acid, stir momentarily with the bulb, step back and (CARE) light the ether as it boils from the tube.**

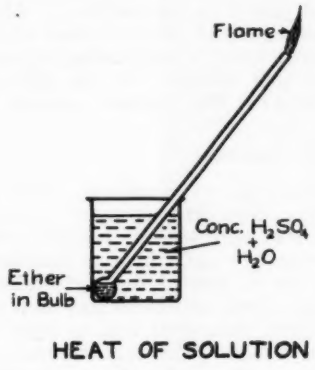

Figure 7-2

*7-3 Set-up as in Figure 7-3. Use lg. granular $KClO_3$+ lg. granulated sugar. **To ignite, add a few drops conc. acid to the chlorate-sugar and**

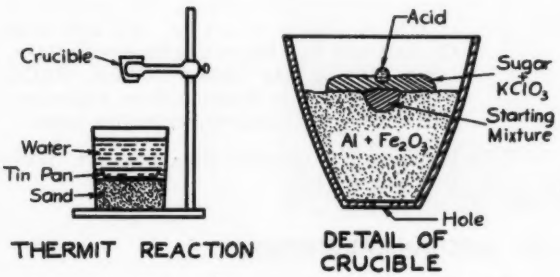

Figure 7-3

step back immediately (CARE). Molten iron splashes around (have fire extinguisher handy), runs through hole in crucible, eats hole in pan under water.

Endothermic reaction

*7-4 NH_4NO_3. 250-ml. beaker, 2 × 2 × 1/8" block of wood, stirring rod. Run a few drops of water on the block of wood, and on it place the beaker filled with NH_4NO_3. **Run in 50 ml. water, stirring well. Beaker freezes to block of wood.**

B. ELECTRICAL ENERGY

Electricity generated

*7-5 See Figure 7-5. Test-tube, Mg ribbon, H_2SO_4-aq., doorbell, one post leading through No. 16 copper wire to a copper spiral about 2" long, 1/2" in diameter, other post leading through copper wire to a battery clip to which is fastened 50 cms. clean Mg ribbon folded in a **bunch. A 250 ml. beaker**

Turn the page for additional demonstrations

*Footnotes

7-2 This is a dramatic way for showing that heat is evolved. Also the lecturer can point out that the mixing is deliberately being carried out the wrong way, i.e., "The water should be in before you add the H-2-S-O-4; or else you might not feel too well—you might not even live to tell."

7-3 The author finds the use of chlorate-sugar-acid preferable to the conventional Mg ribbon method. Be sure to use *granulated* $KClO_3$ and sugar; with powdered ingredients there is a dangerous flare-up. A battery jar or a Pyrex brand jar 12" high and 12" in diameter can be used in place of the pail; the effect, of course, is considerably more dramatic, provided your pocketbook can stand the strain of replacing jars cracked by molten iron.

7-4 Try this before-hand, since it does not work easily. Use hard-wood not porous wood.

7-5 This is an exceptionally instructive experiment. Write the molecular equation, then the ionic equation; show flow of electrons, then carry out the experiment.

7-6 Set up cell but neglect to insert the salt bridge. Proceed as though you expected current to be generated. When it is not, let the class "discover" that the circuit needs the salt bridge to complete the electrical circuit.

7-12 Variations of this follow. (a) Spray method: Fill two perfume atomizers with solutions A and B. Spray the solutions together, carrying this out over the sink so that the solutions fall harmlessly into the sink: a beautiful luminescent cloud is produced. (b) Jar method: Float a lump of ice (to show it is really "cold" light) in a large battery jar filled with water. Simultaneously pour in solution C (1 g. Luminol + 100 ml. NaOH-aq.) and solution D (2.5 g. potassium ferricyanide in 100 ml. 3% H_2O_2). Stir vigorously. (CARE): Perform this behind glass shield to protect your students. P.S. How about you?

Labels for Topic 7. (For code, see instructions for assembling kits, J. Chem. Educ., 32, 12A(1955).) 7-1-*J*-wooden tongue depressors, 7-1-*J*-lump coal, 7-1-*J*-strips of paper, 7-2-*N*-conc. H_2SO_4, 7-2-*d*-ether, 7-3-*J*-thermit, 7-3-*w*-thermit starting mixture, 7-3-*w*-granulated sugar, 7-3-*w*-granular $KClO_3$, 7-3-*d*-conc. H_2SO_4, 7-3-*J*-paper cups, 7-4-*J*-NH_4NO_3, 7-5-*N*-H_2SO_4 aq., 7-5-*J*-Mg ribbon, 7-5-*J*-copper spiral and wire, 7-5-*J*-copper wire with battery clip, 7-6-*J*-Zn rods, 7-6-*J*-1 × 2" foils of Cu, Sn, Al, Ag; 7-6-*N*-NaCl aq., 7-6-*N*-$ZnSO_4$ aq., 7-6-*N*-$CuSO_4$ aq., 7-6-*N*-$SnCl_2$ aq., 7-6-*N*-$AlCl_3$ aq., 7-6-*N*-$AgNO_3$ aq., 7-6-*J*-salt bridge, 7-6-*w*-cotton, 7-7-*N*-$AgNO_3$ aq., 7-7-*N*-$ZnSO_4$ aq., 7-7-*J*-1 × 2" foil of Ag, 7-7-*J*-Zn rods, 7-9-*N*-KI aq., 7-9-*N*-NaCl aq., 7-9-*d*-phenolphthalein solution, 7-10-*w*-Mg ribbon, 7-11-*d*-conc. H_2SO_4, 7-11-*w*-granular $KClO_3$, 7-11-*w*-granulated sugar, 7-11-*w*-$CuCl_2$, 7-11-*w*-$SrCl_2$, 7-12-*w*-Luminol (3-amino-phthal-hydrazid), 7-12-*N*-NaOH aq., 7-12-*w*-potassium ferricyanide, 7-12-*N*-3% H_2O_2, 7-13-*w*-Mg ribbon, 7-13-*N*-$AgNO_3$ aq., 7-13-*N*-NaCl aq., 7-14-*w*-Mg ribbon, 7-17-*J*-$HgBr_2$, 7-17-*J*-KI.

two-thirds full of H_2SO_4 aq. Generate H_2 from Mg and acid; H_2 ignites with pop from match held at mouth of test tube. Suddenly lower copper coil and Mg ribbon into the acid: electric current is generated, bell rings.

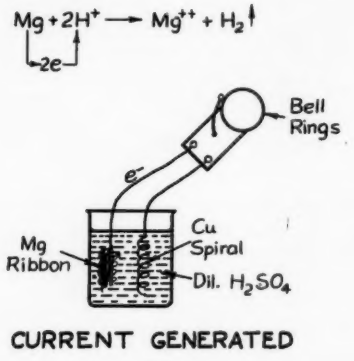

Figure 7-5

*7-6 Zn rod, 1 × 2″ foils of Cu, Sn, Al, Ag; NaCl salt bridge consisting of a U-shaped 6mm tube 20 cms. long filled with NaCl-aq. and stoppered with cotton; $ZnSO_4$-aq., $CuSO_4$-aq., $SnCl_2$-aq., $AlCl_3$-aq., $AgNO_3$-aq.; large galvanometer with copper wire leads with battery clips, five 250 ml. beakers. **Set up cells and generate electricity, for example Zn/Zn^{++}/bridge/Cu^{++}/Cu. Compare the voltage obtained with the positions of the metals in the EMF series.**

7-7 As in 7-6 but using a hydrogen electrode to compare H_2/H^+ $//Zn^{++}$ $/Zn$ with H_2/H^+ $//Ag^+$ $/Ag$.

7-8 **Exhibit:** Cells, batteries.

Electricity consumed

7-9 Repeat 1-4, electrolysis of water; and 4-18, electrolysis of KI.

C. LIGHT ENERGY

Light evolved

7-10 Mg ribbon, forceps, burner. **Ignite, showing light off.**

7-11 Two 6 × 6″ asbestos squares, conc. H_2SO_4, towel. Mix without grinding (CARE) equal volumes of granular $KClO_3$, granulated sugar, and $CuCl_2$. Make another mixture containing $KClO_3$, sugar, and $SrCl_2$. **Add drop of acid to piles (CARE): green and red fire.**

*7-12 Luminol (3-amino-phthal-hydrazide), NaOH-aq. potassium ferricyanide, 3% H_2O_2, two 1-liter beakers, large U-tube, large funnel supported on ring over a 1-liter Erlenemeyer flask, 500 ml. narrow-neck plastic-capped bottle. Solution A: 0.1 g. luminol + 5 ml. NaOH-aq. (5% NaOH) + 1000 ml. water. Solution B: 10 ml. 3% H_2O_2 + 0.25 g. potassium ferricyanide + 1000 ml. water. **Darken room completely. Simultaneously pour Solutions A and B through the funnel: the glowing solution will run down into the Erlenmeyer flask. Pour into the beakers. When glowing begins to fade, restore by adding solid crystals of ferricyanide, or additional NaOH-aq. Pour into the bottle and pass it to the audience. Also pour the glowing liquid into one limb of the U-tube. Soak a towel in the glowing liquid, rinse over the sink (CARE: do not spill on clothes, remember the solution contains NaOH).**

Light consumed

7-13 $AgNO_3$-aq., Mg ribbon, NaCl-aq., filter paper, filter paper on funnel on rack, forceps, burner, two 400-ml. beakers, stirring rod. **Precipitate AgCl, heat to coagulate it, filter it, dry it, spread the AgCl-cake on a dry filter paper, and cover half of it with paper. Expose uncovered half to light of burning Mg ribbon. The exposed half (dark) and unexposed half (white) illustrate photographic process.**

7-14 Mg ribbon, forceps, glove, tanks of H_2 and Cl_2, 18 × 150 mm. test tube full of water clamped inverted in a trough of water so that only the lip of the tube (CARE) is under water; tube covered with protective mantle of fine wire netting. **Fill half with Cl_2, half with H_2. Protecting hand with glove, bring burning Mg ribbon (CARE, FACE AVERTED) up to tube: violent explosion, HCl gas forms, dissolves, water fills tube.**

7-15 **Exhibit:** photographic film, negative, positive, colored film.

D. MECHANICAL ENERGY

7-16 *Energy evolved.* Repeat 1-7, exploding a pop-bottle of $2H_2 + O_2$.

7-17 *Energy consumed.* $HgBr_2$, KI, mortar and pestle. **Grind white solids: orange HgI_2 forms.**

Next month's Tested Demonstrations in General Chemistry

8. EQUILIBRIUM. OXIDATION AND REDUCTION

For a complete list of topics for 1955–6 see J. Chem. Educ., 32, 28–9(1955)

Portable Oven from Third Millenium B.C.

(See page 356)

A Durable, Highly Sensitive, Low-Cost Welch Balance of Excellent Accuracy

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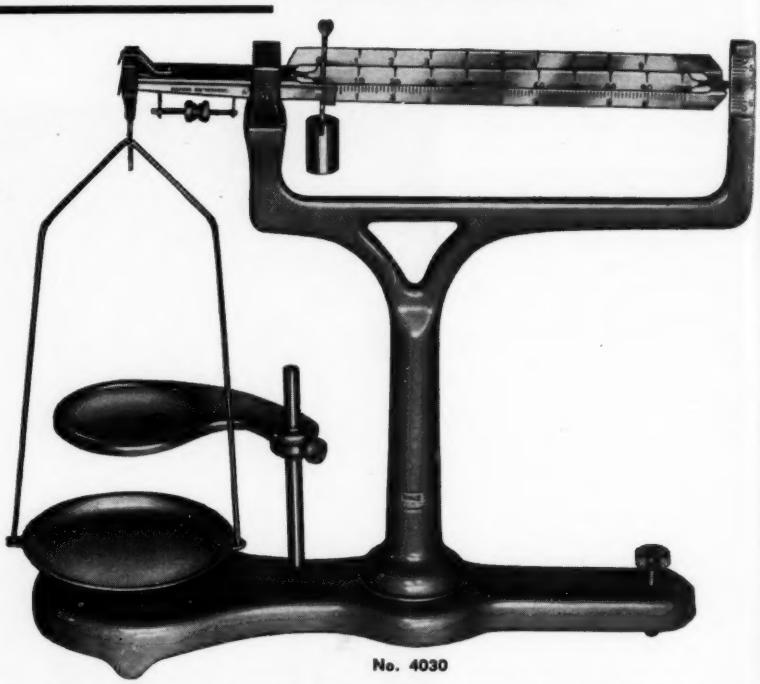

No. 4030

4030. TRIPLE-BEAM BALANCE, High Form. This balance is recommended for weighing chemicals, measuring specific gravity, and for general laboratory use wherever high sensitivity is required. It reads directly to 0.01 gram and is sensitive to load changes smaller than this. Its capacity is 111 grams and using the auxiliary weight listed below, the capacity can be increased to 201 grams.

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Editor's Outlook

UNLESS the prospects of a scientific career include the spirit of freedom, we are unlikely to attract to it the kind of young man or woman who in the long run will pursue it most effectively and productively.

There is no doubt but that most of those who think they hanker after science are really being lured by technology. Most of our talk about the wonders of science really concerns its *results*—gadgets, labor-saving devices, and aids to soft living. All of which are commendable, to be sure, for they permit us to live not only in more luxurious softness but also more happily and abundantly.

But there is a more permanent attraction in science than its tangible returns. No doubt the man whose scientific brainchild is no more than a "black box" gets his greatest satisfaction not from the box itself, nor from his remuneration for having made it, but from the creative thrill of accomplishing something that had never been done before. I am told that even the tycoons of high finance are urged into their million-dollar "deals" not so much by slimy greed or desire for power over their fellows as by thoughts of creative accomplishment. Of course I wouldn't know; such operations are on another planet, as far as I am concerned!

Dr. C. A. Thomas, president of the Monsanto Chemical Company, recently delivered the A. D. Little Memorial Lecture at the Massachusetts Institute of Technology, on the subject: "Creativity and Science." He pointed out that the creative aspect of science combines the practical and the ideal, and that upon this depends our national welfare, even our national existence. This is the intensely personal appeal of science, for it stirs the personal emotions. The strength of the appeal of science to the individual is in its spirit of freedom—freedom to create. Unless this is uppermost, there is nothing in science for the individual.

According to Dr. Thomas, science students of the future must be taught to realize that:

> . . .pragmatism, the rigid code of practicality, is a good professional framework for some . . . but it may be unacceptable to others. From undergraduate training upward—and it cannot be started too early—students of the sciences should be made to appreciate that some men are driven by a deep desire to add to the store of knowledge, that the challenge of discovery is rewarding whether it has immediate practical value or not . . . and that this, too, is good and right. Whatever path the science student chooses . . . he must be conditioned to realize that his choice is made on the basis of personal preference, with the firm conviction that neither the one nor the other is a superior calling.

In certain circles today science is mistrusted. This attitude fails to realize the true, creative function of science, but judges it in terms of whether or not it is "useful." The greatest *creation* of all—the human spirit—is scarcely "useful."

An old letter file a few days ago revealed a suggestion that had been gathering dust since 1946. Said a correspondent: "I should like to congratulate the JOURNAL and Dr. Lauffer on the final paragraph of the article 'Influenza virus' which appears on page 537 of the November, 1946, issue of the JOURNAL. . . . I hope that you will reprint parts of this paragraph in a later issue." So we do so.

> The conquest of influenza, important as it is in terms of human welfare, has been a by-product of basic scientific studies directed principally toward discovering the nature of viruses in general. . . . This feat was made possible by the experience amassed in the purification and crystallization of other biologically active proteins, particularly the enzymes. Yet who would have dreamed that the crystallization of urease and pepsin opened the way to the conquest of influenza? Such things come under the heading of useless academic research.

So after all, what is important, what is useful? Only the urge to discover, to create, for its own sake.

A NOTATION FOR THE STUDY OF CERTAIN STEREOCHEMICAL PROBLEMS

MELVIN S. NEWMAN
Ohio State University, Columbus, Ohio

For many years the Fischer projection formulas have been used to represent the stereochemistry of molecules with multiple asymmetric centers. These formulas are adequate if one is dealing only with the classical aspects of stereoisomerism. Recently, however, the investigations involving conformational analysis have required other notations for visualization of the fine points. The author has been using a different kind of notation for several years for problems involving compounds containing two adjacent asymmetric carbons (*1*). Recently this notation has been extended to cover similar problems in cyclohexane and related compounds. This article describes some applications of the notation to various stereochemical problems.

To be specific, let us consider the isomers of a 1,2-dibromide having two similar asymmetric carbons, RCHBrCHBrR. The projection formula written is that envisioned when the eye is placed along the extension of the bond joining the two asymmetric carbons. As a convention the carbon farthest from the eye is called carbon 2, and that nearest, carbon 1. Carbon 2 is designated by a circle with three equally spaced radial extensions to locate the three other atoms to which it is attached. Carbon 1 is designated by equally spaced radii, as shown in Figure 1.

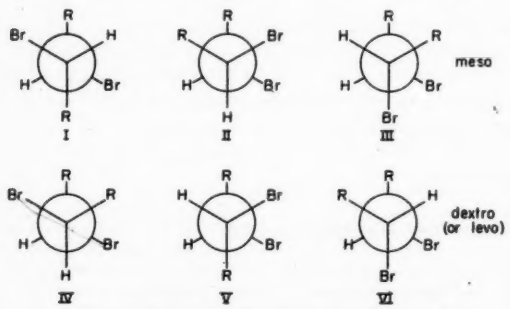


Figure 1. Rotamers of Diastereomeric Dibromides

If one bears in mind the fact that the valence bonds to carbon 1 are viewed as one views the spokes of an umbrella when the eye is at the handle, and the valence bonds to carbon 2 are viewed as though the eye were at the tip, it is simple to write a *meso* form. One writes the three different groups in the same clockwise order for each carbon; *i. e.*, in the present example, R, Br, H. This assures one that the configuration at the two carbons is opposite, and hence a *meso* form is at hand. To write a *d* or an *l* form one has merely to interchange any two groups on either atom.

The structures in Figure 1 are written in staggered forms corresponding to the three low-energy conformations. For convenience these forms will be called rotamers (*2*). By inspection of these structures it is possible to make predictions as to the stereochemistry and rate of a number of reactions as shown below.

PREDICTION OF GEOMETRIC ISOMERS OBTAINED ON DEBROMINATION OF VICINAL DIBROMIDES

Consider the rotamers of a *meso* dibromide I, II, III, and those of the corresponding *d* or *l* dibromide, IV, V, and VI.

Assuming that the two bromine atoms are *trans* eliminated it can readily be seen that a *trans* olefin will result from rotamer I, *meso* form, and that a *cis* olefin will result from rotamer IV, *dextro* (or *levo*) form. Of course, rotamers II and III will yield the same product as I, and V and VI the same as IV.

PREDICTION AS TO RELATIVE RATES OF FORMATION OF PRODUCT FROM DIASTEREOISOMERS

Three methods may be used to predict the relative rates of reaction of diastereoisomers. Each method is offered here as being empirical. It should be emphasized that in the application of any method an assumption must be made as to whether the reaction under consideration requires a *cis* or *trans* involvement of the groups undergoing reaction. In this case, for example, the assumption is made that the two bromine atoms are removed (using either zinc and alcohol or sodium iodide in acetone) when in the *trans* position.

Method 1. Estimation of the Steric Factors on the Stability of the Products Formed

The essence of this method is to predict a greater rate of reaction for that isomer which yields the more stable final product. Ordinarily the *trans* olefin is presumed to be more stable than the *cis* olefin, hence the *meso* form should react more rapidly than the *dl* form. Furthermore, the larger the groups which end up *cis* or *trans*, the greater should be the ratio of rates. Experimentally the following relative rates have been determined for the debromination using iodide ion: *meso*-2,3-dibromobutane, 0.065, *dl*-2,3-dibromobutane (*3*), 0.035; *meso*-dibromohexane, 0.154, *dl*-2,3-dibromohexane (*4*), 0.044; and *meso*-dibromooctane, 0.183, *dl*-dibromooctane (*4*), 0.060. A qualitative comparison of the isomeric stilbene dibromides indicated that the

meso form reacted at least 100 times as rapidly as the *dl* form. Thus it is seen that there is a larger ratio of rates in the molecules where larger groups produce the major steric effects than in the molecules where methyl groups provide the interference.

Method 2. Comparison of the Relative Abundance of the "Reactive" Rotamers

Example 1. The essence of this method of prediction is to compare rotamers I and IV with respect to their relative abundance in the rotamer mixture. In the *meso* form, I, the rotamer containing the bromine atoms in the *trans* position also has the R groups distant from each other. In the racemate, IV, the rotamer containing the bromine atoms in the *trans* position has the R groups close together and in close juxtaposition to the bromine atoms also. Hence one could argue that the *meso* form on the time average approximates I more nearly than the racemate approximates IV. Therefore the *meso* form should react more rapidly than the racemate (which is the case). It is realized that this argument may be based on unsound principles. Nevertheless, the predictions based on it have been correct in every case examined to date.

It is interesting to note that the Br—Br distances in *meso* and racemic dibromostilbene (solid state) have been determined by X-ray diffraction (*5*). The distance for the meso form is 4.50 Å., corresponding to the geometry of rotamer I (R = C_6H_5), whereas the distance for the racemic form is 3.85 Å., which is about as close as the van der Waals radius for bromine will allow two bromines to approach. On the other hand, measurements on the *meso* and racemic forms of 2,3-dibromobutane (liquid state) show that the bromines are essentially *trans* in both forms (*6*), as the Br—Br distance is about 4.60 Å. in each.

In cases where the stability of the two possible products is not known, Method 1 of predicting the relative rates for diastereoisomers cannot be applied unless one makes an assumption about the stabilities of the end products. However, Method 2 can still be applied as shown below.

Example 2. Prediction of Relative Rates of Reaction of Diastereomeric Glycols to Form Cyclic Ketals. Consider the rotamers of the *meso* and racemic forms of hydrobenzoin, (see Figure 2). The reaction under consideration is the formation of a cyclic ketal using acetone:

$$C_6H_5CHOHCHOHC_6H_5 + CH_3COCH_3 \xrightarrow{H^+} C_6H_5CH\underset{\displaystyle O}{\overset{\displaystyle O}{<}}\!\!>\!\!C(CH_3)_2 + H_2O$$

The assumption is made that the reaction involves a *cis* arrangement of hydroxyl groups because the final ketal contains a five-atom heterocycle involving the two oxygens. On the time average rotamer IX of the *meso* form would be favored because of steric factors, and rotamer XII of the *d* (or *l*) form. Since XII has the favored *cis* location of hydroxyl groups whereas IX does not, it would be predicted that the racemate would react more rapidly than the *meso* form. The relative experimental rates are: racemate 38.8; *meso*, 4.4 (*7*).

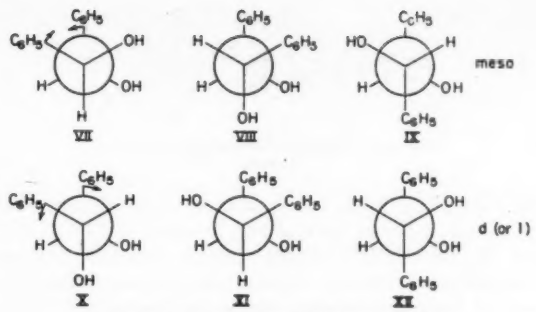


Figure 2. Stereoisomeric Hydrobenzoins

Method 3

Perhaps the best method of predicting relative rates in this and similar cases is to note whether the large groups approach each other or move farther away in going from reactant to the activated state. By observation of any one of the rotamers VII, VIII, or IX, it can be seen that in going to the cyclic ketal the phenyl groups must approach each other rather closely. In the case of rotamers X, XI, and XII, it is seen that the phenyl groups move to a position farther apart. Note particularly the small arrows in rotamers VII and X, which indicate the direction in which the phenyl groups move during approach to the activated state. The prediction in such cases is that the isomer in which the large groups move away from each other in going from reactant to product will react more rapidly than that in which the large groups move toward each other. In other words, that isomer which forms the most strained activated state will be the one which reacts at the slower rate.

PREDICTION OF MIGRATING GROUP IN THE CASE OF DIASTEREOMERIC AMINO ALCOHOLS

In semipinacolic deaminations an amino alcohol,

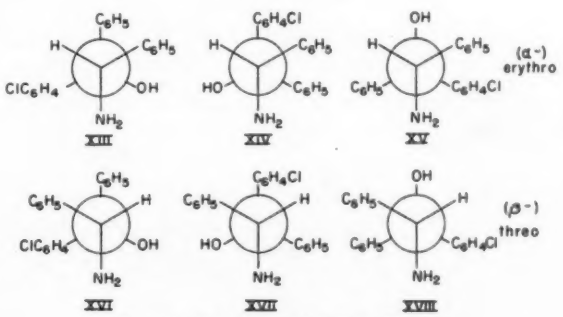


Figure 3. Stereoisomeric Amino Alcohols

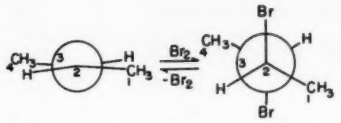


Figure 4. Addition of Bromine to *Trans*-2-butene

$RR'COHCHR''NH_2$, on treatment with nitrous acid may yield either or both of two ketones, R'COCHRR'' and RCOCHR'R''. From certain studies (*8*) on "migration aptitudes" it might be supposed that the ratio of these two ketones would depend on the migration aptitudes of R and R'. However, recent studies

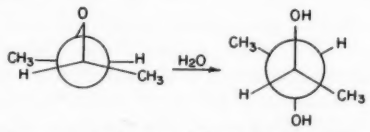


Figure 5. Hydration of *Trans*-2-butene Oxide

(*9*) have shown that the ketone formed depends mainly on the stereochemical configuration of the amino alcohols and not on the electronic nature of the migrating group. Results like these are readily understood by a study of the rotamers shown in Figure 3.

In the rearrangement that occurs when the amino alcohol is treated with nitrous acid, it is assumed that the group which displaces the amino group does so with inversion. This assumption has been proved correct

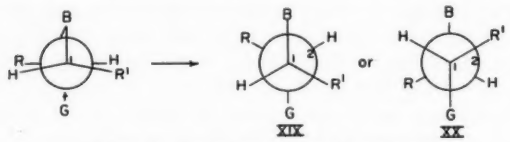


Figure 6. Cyclic Intermediate Reactions

in one case (*10*) and is probably generally valid. Curtin and his co-workers (*9*) showed that the α-isomer of 1,2-diphenyl-1-*p*-chlorophenyl-2-aminoethanol yielded *p*-chlorophenyl benzhydryl ketone almost exclusively (phenyl migration), whereas the β-isomer yielded only α-*p*-chlorophenyldesoxybenzoin (*p*-chlorophenyl migration). Of the rotamers XIII, XIV, and XV: XIII would lead to phenyl migration; XIV would lead to *p*-chlorophenyl migration; and XV would probably lead to products other than the rearranged ketones. Since rotamer XIII should be favored for steric reasons over XIV, the α-isomer should react mainly with phenyl migration (as it does). By similar reasoning it is seen that the favored rotamer, XVII, should lead to *p*-chlorophenyl migration in the β-series (as it does). The configurations for the α-(erythro) and β-(threo) isomers were established unequivocally (*9*).

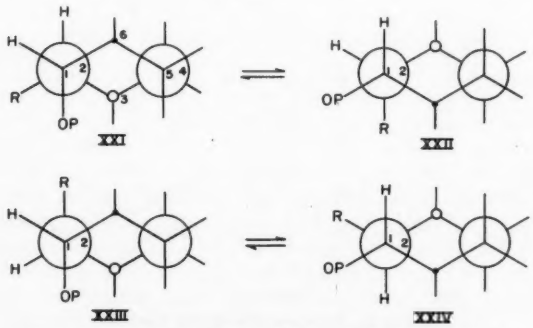


Figure 7. Rotamers of *Cis*- and *Trans*-2-alkylcyclohexanols

In order to allow for the representation of stereospecific additions to olefinic linkages the notation shown in Figure 4 is recommended. Here the eye is looking at carbons 2 and 3 of *trans*-2-butene from the plane containing the doubly bonded atoms. The bonds connecting the CH_3 and H groups to these carbons are bent slightly to allow both sets to be seen. The final dibromide is recognized as *meso* since the clockwise order of groups is the same (CH_3, H, Br) on both carbons from the eye position (*vide infra*). Similarly it can be shown that *d* (or *l*) and *l* (or *d*) forms result from *trans* addition of bromine to *cis*-2-butene according to the direction, above or below the plane, of approach of bromine to carbon 2.

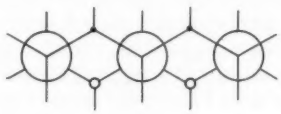
By a modification it also is possible to follow the course of other stereospecific reactions involving three atom ring compounds, such as ethylene oxides, ethylenimines, and ethylene sulfides, or bridged ions, such as those postulated in reactions with neighboring group participation, *e. g.*, acetoxy, methoxy, phenyl, etc. In Figure 5 the hydration of *trans*-2-butene oxide to yield *meso*-2,3-butanediol is illustrated.

The problem of notation for hypothetical reaction intermediates involving bridged ions is more difficult. However, if one breaks down this problem into two parts, each may be solved in a satisfactory manner. The first part is the indication of the nature of the bridged intermediate. The second part is the indication of the stereochemical relationships of the products formed when the bridged intermediate is attacked by some reagent at each carbon respectively. Different representations for bridged ions have been used by Winstein (*11*), Cram (*12*), Curtin (*9*), and Roberts (*13*) depending upon the species at hand. The type of notation illustrated by Figure 6 is recommended for explanation or prediction of the products formed from such bridged intermediates. The only bond not seen when this notation is used is that joining the two carbons that are connected by the bridging group. Since the unseen bond is not affected during reaction one is not sacrificing much. As before, the circle represents the carbon farthest from the eye, and the radii meeting in the center, the carbon nearest the eye. *B* represents any bridging structure and *G* any attacking group. If desired more detailed (slightly perspective) drawings for *B* are possible. If the attack is on carbon 2 isomer XIX is obtained, whereas attack at carbon 1 produces isomer XX.

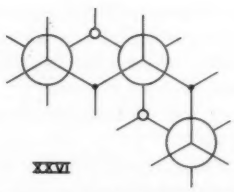
This notation may advantageously be extended to illustrate stereochemical points in cyclic structures as shown in Figure 7. For example, differences in the

rates of alkaline hydrolysis of the half phthalates of *cis*- and *trans*-2-alkylcyclohexanols (*14*) may be rationalized rather easily. Structures XXI through XXIV represent stereoisomeric and rotameric forms of the half phthalates (*OP*) of 2-alkylcyclohexanols. Carbon 1 of the cyclohexanols is represented by the three radii, and carbon 2 (containing the alkyl groups R) is represented by the circle with the three radial extensions. The other atoms in the ring are designated by the small numbers 3, 4, 5, and 6 in structure XXI. There are four bonds which are not seen in this notation: One is an equatorial bond pointing directly at the reader from carbon 6; a second is an equatorial bond on carbon 3 pointing directly away from the reader. The convention adopted for these cases uses for an unseen bond pointed toward the eye and for an unseen bond pointing away from the eye. The fact that both of these unseen bonds are equatorial partly overcomes the objectionable feature of this notation. The other two bonds not seen are those connecting carbon 1 with 2, and 4 with 5.

If one makes the assumption that the saponification step always occurs when the ester bond is equatorial, one can readily see that the steric relationship be-



XXV

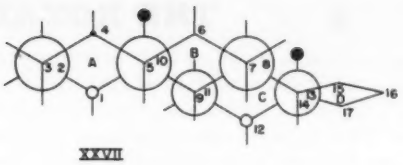


XXVI

Figure 8. *Trans*-decalin (Above) and *Cis*-decalin (Below)

tween the ester group and the alkyl group on carbon 2 is the same (approximately) in both the *cis* form, XXII, and the *trans* form, XXIV. However, form XXIV has R in an equatorial position whereas form XXII has R in an axial position. Hence one would expect to find a greater energy difference between the ground state and the activated state for XXII than for XXIV and hence the *cis* isomer should be saponified more slowly than the *trans* (as is the case) (*14*).

Finally, the utility of this notation can be illustrated by inspection of the formulas for *trans*-decalin, XXV, *cis*-decalin, XXVI, the steroid nucleus with A-B rings *trans*, XXVII and XXVIII (two views), and *cis*, XXIX and XXX (two views). With a little practice it becomes a simple matter to see whether a bond is α or β, equatorial or axial.



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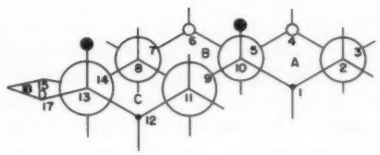

XXVIII

Figure 9. Steroid Nucleus A-B Rings *Trans*

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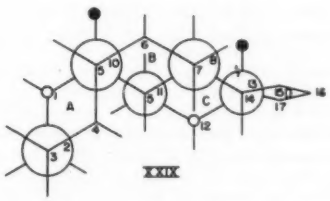
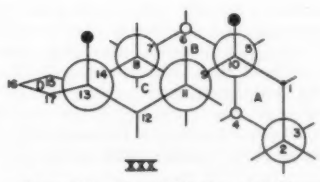


XXIX



XXX

Figure 10. Steroid Nucleus A-B Rings *Cis*

THE ROYAL CORK INSTITUTION

MARGARET MacSWEENEY and JOSEPH REILLY
University College, Cork, Ireland

IN THE history of science, regional institutes deserve special mention. During the nineteenth century their work paved the way for the entry of the experimental sciences into general education and bridged the gap between school and university. Where records have been preserved interesting links with current activities may be traced.

The Royal Cork Institution,[1] an early example of such an establishment, is of particular chemical interest because of the work carried out there by the distinguished nineteenth-century chemist Edmund Davy (1785–1857). The institution was concerned with some aspects of chemical education as early as 1803. In 1813 there was founded in it a school of chemical education which has been connected with chemical endeavor up to the present day, though not now under the name of the RCI.

BACKGROUND

Cork, the second city in Ireland 150 years ago, was a prosperous, mercantile port with a valuable export trade principally in dairy products and salted meat. The main reasons for the rise of a scientific institute there at that date were educational needs and the example of other societies.

The advantages of the one Irish university, located in Dublin, were unattainable for many in the provinces because of religious tests or for reasons of expense. Under university level centers such as Cork had excellent academies, but their curricula were preponderantly classical and fees were large.[2]

Toward the close of the eighteenth century the necessity for increased facilities for higher education began to be recognized. In 1791 the establishment of a professional academy, or a number of them, was proposed in the "Commissioners of Irish Education Inquiry Report."[3] The report resulted in no educational enactment. But the facts which conditioned its proposals had their own force, and the activities which led to the establishment of the RCI were mainly due to a Presbyterian clergyman and schoolmaster, Thomas Dix Hincks (1767–1857), son of English parents, who had moved to Dublin in the year of his birth.

THOMAS DIX HINCKS

Before he found his vocation for the ministry Hincks had been apprenticed to an apothecary. Another reason for his interest in science was the fact that toward the close of the eighteenth century scientific findings were providing an abundance of arguments against revealed religion for some pamphleteers. Hincks was the author of a series of letters addressed to his fellow citizens in 1795, "Occasioned by the circulation of a work entitled, 'The Age of Reason.' " In these letters he quotes extensively from the writings of Joseph Priestley.

The foundation of the institution was also encouraged by the example of existing societies such as the Royal Dublin Society and in particular the Royal Institution, London (founded 1799), whose objects at that time were eminently practical.

Three stages may be distinguished in the early growth of the institution.

(1) In 1802 Hincks proposed to conduct a course of public scientific lectures.

(2) Prominent citizens subscribed funds for the necessary equipment for his demonstrations, retaining proprietorial rights in the collection.

(3) In 1807 premises were fitted up with a library, laboratory, mineralogical collection, etc; the RCI was incorporated by Royal Charter and allotted a parliamentary grant of £2000 a year.

FIRST COURSES

The first courses were mainly, but not exclusively scientific. The syllabus[4] makes quaint reading now. The preface stated with modesty and candor:

[1] This account of the Royal Cork Institution (designated the RCI in this paper for brevity) has in addition to contemporary references the following sources. (1) A minute book of the institution (1826–61). This hitherto unstudied folio (450 f/c pages) comprises the minutes of managers' and proprietors' meetings. Early records in the book bear the signature of Edmund Davy, professor of chemistry and for a time secretary. (2) A library catalogue (1824). (3) A syllabus (1803) of the first course of scientific lectures delivered in the institution (the first in Cork city). These three references are in the library of University College, Cork.

[2] William Thompson, a founder proprietor of the RCI, wrote that: "Even gentlemen and merchants," with £1000 a year were "distressed" by the expense of educating their families. Boarding schools charged from £40 to £100 a year and the middle classes could rarely afford to give their children "anything more than a school education of writing, arithmetic and enough Latin to be useless." See PANKHURST, RICHARD K. P., "William Thompson," Watts and Co., London, **1953**, p. 10.

[3] CORCORAN, T., "State Policy in Irish Education," Longmans, Green and Co., London, **1916**, p. 173.

[4] "A syllabus of a course of lectures delivered in the year 1803 by T. D. Hincks, M.R.I.A., Lecturer in the Cork Institution for the diffusion of knowledge."

All that was aimed at was to illustrate and explain what has been taught by others and to refer to those works where more complete information may be obtained.

Modest is not the word for the scope of the course. A Homeric task was proposed for lecturer and listeners, though the arrangement of the lectures had much to recommend it. They proceeded through language, literature, reasoning, and elementary mathematics, to science proper. The subjects included: natural history, matter and its properties, sound, gases, alkalies and acids, earths, metals, fixed stars, planets, comets, history, electricity, hydrostatics, mechanics, and the evidences of natural and revealed religion. Many instruments and simple machines were described and illustrated as far as the apparatus permitted. The account of the common gases does not widely differ, except in the absence of chemical equations and in nomenclature, from that given in elementary chemistry lessons of a much later date; that of acids, alkalies, and salts, in the light of then current chemical knowledge, is unexceptional. Electricity, at the time a highly novel study,[5] was touched on. The Leyden jar and the simple electric battery were described, and serious students referred to "Mr. Davy's syllabus of lectures at the Royal Institution of Great Britain," while the general reader was directed to "a short and clear account... published by Dr. Meade of this city."

Considering the general state of scientific knowledge in 1803 the course provided a remarkable series of public lectures for an Irish provincial city. Slow communications made Cork exceedingly remote from even the nearest schools of science—Dublin, Edinburgh, London. It may be questioned whether any comparable center in the British Isles showed an equally up-to-date and active interest in science at so early a date. This almost back-door entry of the natural sciences into general education via public lectures and societies sponsored by enthusiasts was similar to the pattern of advance in much larger centers.

The founder-proprietors[6] formed a representative cross section of the local notables. Among them were the Earls of Cork and Shannon,[7] other noblemen, clergymen, professional men, bankers, and merchants.

The presence of a few Catholics among the proprietors, more than 20 years before the emancipation act relieved the Catholics of Ireland and England of many educational and civic disadvantages, shows the liberal spirit of the institution's founders.

EARLY RESOURCES AND GROWTH

The course of lectures delivered in 1803 was repeated in 1804 and 1805. In 1806 wider and more specialized courses were started in chemistry, natural philosophy, natural history, and agriculture. The last was a practical program of studies in a center like Cork whose commercial prosperity was then (as now) closely connected with its extensive agricultural hinterland.

In the summer of 1806 the establishment of a scientific library and a botanic garden was discussed by the proprietors. These undertakings demanded resources larger than could be obtained by public subscription. An appeal was made to the Lord Lieutenant[8] and the Chancellor of the Irish Exchequer resulting in a parliamentary grant of £2000 to the institution. The Lord Lieutenant further recommended that it be made a corporation by royal charter, and this was done in 1807.

Purposes other than teaching were indicated:

It is proposed to have stated meetings of the proprietors and of such scientific men as may be admitted by them for the purpose of discussing philosophical subjects; and committees will be occasionally formed for conducting any experiments which may be thought desirable for ascertaining any interesting facts.[9]

Thus, it is not surprising that the RCI found enthusiastic supporters among those who lacked a center where they could exchange ideas with men of similar interests, and where there were laboratory facilities, apparatus, and a scientific library. Medical men, antiquarians, enlightened manufacturers, and doubtless the normal quota of dilettanti and cranks became members. Eight years after the first course of lectures the institution had developed a scheme for the encouragement of scientific agriculture. It was publishing a quarterly journal and had established four professorships: chemistry, natural philosophy, natural history, and agriculture. These results had been achieved with limited material equipment but an unstinted expenditure of human energy and enthusiasm.

The balance sheet of the RCI for 1806–07 (reproduced in Day's paper[6]) gives an idea of the resources then considered adequate for a small scientific institute. The total subscribed came to two thousand guineas, most of which was invested in three and one-half per cent stock. In that first year of the corporation the parliamentary grant was expended almost entirely on apparatus, fitting up of a lecture room and laboratory, library books, and rent.

ORGANIZATION

The RCI was organized[10] on the lines of the Royal Institution of London, with various differences because of its limited resources and aims. The second minute book shows it to have been a well run educational institution whose affairs were guided by a board of managers. At the annual general meetings of the proprietors

[5] Almost 30 years before the publication of Faraday's "Experimental Researches in Electricity, 1831–38," London, 1839.

[6] A list of 45 original proprietors and a later list of 78 names is given in a paper by Day, R., *J. Cork Historical and Archaeological Soc.*, **12**, 44 (1906).

[7] Descendants of Richard Boyle, first Earl of Cork and father of the Hon. Robert Boyle, F.R.S., co-discoverer of Boyle's law.

[8] The 6th Duke of Bedford, renowned for his interest in scientific agriculture.

[9] From *The Athenaeum*, May 1, 1807. Quoted in *J. Cork Historical and Archaeological Soc.*, **41**, 57–8 (1936).

[10] It must be assumed that the procedure during the early years (1803—or 1807 if records only began after the incorporation—to 1826) was similar to that followed after 1826 because up to now the first minute book has not come to light.

ten managers were elected for a tenure of office of three (occasionally two or one) years. This insured both continuity and some annual changes on the board. A treasurer, auditors, and a secretary were appointed by the proprietors. The board of management chose five committees: science, fine arts, library, accounts, and botanic garden. These committees sent reports to the board as occasion arose. The managers held monthly meetings and the minutes of these form the bulk of the second minute book. The proprietors held annual or extraordinary meetings, minutes of which are also recorded.

Lectures were given in the morning and evening and admission was by ticket. The proceeds of the sale of tickets were a perquisite of the lecturers. This arrangement makes it impossible to judge the number or status of the students who attended the courses. Edmund Davy refers to facts which he demonstrated to "my students in the Royal Cork Institution and the Royal Dublin Society." This suggests that the teaching methods were demonstrative rather than practical.[11]

A botanic garden was laid out sometime between 1806 and 1809. Experiments were conducted there with a view to the introduction of crop varieties particularly suited to the climatic and soil conditions of the district.

EDMUND DAVY

Possibly the best indication of the high standing of the RCI is the fact that in 1813 Edmund Davy accepted its professorship of chemistry, after having been assistant to his first cousin, Sir Humphry Davy, in the Royal Institution of London between 1808 and 1812. He remained in the institution for thirteen years and for part of that time combined the duties of professor and secretary.

Russell[12] has pointed out that there is no mention of Edmund Davy in either Paris' or John Davy's biography of Sir Humphry Davy. In the later "Fragmentary Remains," however, one may read in a letter from Humphry Davy to his mother, dated October 5, 1808:

> What I should propose is this, that he [John Davy] and my cousin Edmund should mess together when I am not at the Institution. Edmund will teach him economy which is a very great virtue, and I will endeavour to teach him chemistry and philosophy. Edmund lives very respectably upon sixty pounds a year looking forward to a better salary; but he has his coals, candles, meat dressed, attendance and all those things.[13]

The better salary came to Edmund in the RCI (£100 a year) and Ireland may well have appeared an enlightened nation to him when he quitted the Royal Institution of London to take up his post in Cork. Humphry Davy had been accorded a tumultuous welcome, academic honor, and most generous financial rewards when he lectured in Dublin in 1810–11. Yet Edmund's move (as well as the confusion resulting from the contemporaneous work of his first cousins, Sir Humphry Davy and Dr. John Davy, pointed out by Russell[12]) must be considered contributory to the neglect of his work—even his important discovery of acetylene—by chemical historians. His obscurity may be as much a matter of geography as of family name.[14]

Even the short outline of Edmund Davy's work given in Russell's paper shows its variety and indicates some of the reasons for his interest in various chemical problems. But he was no mere follower of his famous relatives; he possessed ample originality and initiative. His attention to the work of Sir Humphry and Dr. John Davy was a matter of affectionate loyalty between members of a family who were renowned for this quality as well as for their scientific achievements. Edmund Davy had not the versatile genius which has made his cousin Humphry possibly the most "written-up" of all British scientists. Yet he was a fine chemist.[15] While in Cork he kept up a high output of publications on pure chemical research while applying himself when necessity demanded to the scientific examination of problems of public importance. His first paper from the Cork Institution was communicated to the Royal Society in 1817 by Sir Humphry Davy and was entitled: "On a new fulminating platinum."[16] It described the preparation, reactions, and analysis of an explosive compound of platinum which he had studied in Cork. His description of it closely tallies with that of the explosive ammoniacal compound of platinum,[17] $NH_3Pt_2(OH)_{10}$. He recorded his failure to obtain carbon dioxide from the compound and noted the production of moisture in its explosive decomposition. The first observation suggests (as is confirmed by later work of his) that he was curious about the relations between the fulminates and other explosive chemical compounds; the second illustrates his accurate experimental methods and lucid recording of results.

His conclusion that "Fulminating platinum is a triple compound consisting of oxide of platinum, ammonia, and water," indicates that at that date he accepted the theory that complex chemical compounds may be formed by union of simple ones. He showed too that his "fulminating platinum" was more closely related to "fulminating gold"[18] than to "fulminating silver," later characterized[19] as Ag_2N or Ag_2NH. The preparation of platinum black concluded his work on the platinum compounds.

In 1816 and 1817 exceptionally bad weather, resulting

[11] DAVY, E., *Phil. Trans.*, **1831**, pp. 147–64, and *J. Royal Dublin Soc.*, **1856–57**, pp. 62–72.

[12] RUSSELL, J., J. CHEM. EDUC., **30**, 302 (1953).

[13] DAVY, JOHN, "Fragmentary Remains, Literary and Scientific of Sir Humphry Davy, Bart." Churchill, London, **1858**, p. 71.

[14] Berthelot, who in 1859 synthesized acetylene and claimed to be its discoverer, later withdrew the claim (*Ann. chim.*, **68**, 53 (1863)).

[15] KENDALL, JAMES, in "Humphry Davy," Faber and Faber, London, **1953**, p. 77, describes Edmund as: "A scientific Humphry Davy in miniature."

[16] *Phil. Trans.*, **1817**, pp. 136–57.

[17] FRIEND, J. N., "A Text-book of Inorganic Chemistry," Griffin, and Co., London, **1920**, Vol. 9, part 1, p. 297.

[18] "An ammine possibly of composition $[Au(NH_3)_2(OH)_2]OH$," *ibid.*, **1928**, Vol. 10, p. 41.

[19] Raschig, F., *Ann.*, **233**, 93 (1886).

inferior grain harvests, and unpalatable bread caused distress among the poorest sections of the community, while primitive sanitation and incomplete drainage added to overcrowding and malnutrition and caused an epidemic of a particularly virulent fever. Two papers on methods of improving the flour and bread by the addition of various agents[20] and an attempt to analyze the air in the Fever Hospital[21] while it was crowded with patients[22] record Edmund Davy's praiseworthy efforts to put his scientific training and knowledge at the service of his adopted city. He also examined hard water from a local artesian well,[23] and devised a lactometer[24]—a link with the town's dairying industries.

His pure chemical research at this stage was represented by his work on the platinum compounds, an examination of the excretions of the boa constrictor,[25] and a paper on the action of iodine on oils.[26]

SCIENTIFIC AGRICULTURE

A major undertaking of the institution had begun in 1811 with the publication of a journal entitled *The Munster Farmers' Magazine.* Its object was to extend the advantages of the institution to the agricultural community and encourage an interest in scientific experiments in farming. The preface to the first issue of the magazine stated that ". . .the improvement of agriculture. . . as of every other art, must depend on the diffusion and application of science. . . ."[27]

The magazine's practical suggestions were enlightened. Cork was in the lead in scientific agricultural education. In 1830, as quoted by Clow and Clow,[28] it could be said of professorships of agriculture outside Scotland:

> There is one in Dublin, supported by the Royal Dublin Society, one in Cork; and one is destined to be established at some future date in Oxford.

As Liebig pointed out, agriculture is both a science and an art. Contributions to the magazine were on the art rather than the science. But it was in publication a full 20 years before Liebig's "Report on Organic Chemistry" (later published as "Chemistry in its applications to Agriculture and Physiology") heralded the era of systematic agricultural chemistry. It antedated by a year or two Sir John Sinclair's[29] "An account of the systems of husbandry of Scotland," (1814) in which he advocated experimental farming.

The magazine provided a useful service. It contained abstracts of such agricultural publications as existed at that period and gave much local information.

THE LIBRARY

An extant catalogue of the institution's library, printed in 1824, yields some information about progress during the years for which no minutes are available. The books number 2000, with 700 later additions written into the catalogue. The library committee for 1823–24 had three medical doctors and a total of six members. Not surprisingly, medical books form the largest section. Agriculture, chemistry, natural history, natural philosophy, history, philology, and general literature make up the other sections. In the 60-page catalogue the last three sections occupy only 15 pages, showing that during 20 years of growth the RCI remained faithful to its declared scientific purposes.

The periodical literature was excellent. It included the *Phil. Trans.;* the *Ann. Chim.; Trans. Roy. Irish Acad.; Trans. Roy. Soc., Edinburgh; J. Roy. Inst. Great Britain.*

The chemical section had books by Berthollet, Dalton, Humphry Davy, Gay-Lussac and Thenard, William Henry, Lavoisier, Madame Marcet, Nicholson, and Priestley. Later additions included books by Faraday, Liebig, and Thompson.

Cork city had had a good subscription library since 1792, but no general library could provide such a range of specialized, scientific literature as that housed in the institution after 20 years of development. The extant minutes bear witness that one of the most frequent items on the agendas of managers' meetings were proposals of subscribers to the library.

THE INSTITUTION, 1826–31

As the RCI approached its third decade those of its founders who still survived must have felt a well merited sense of achievement. For more than 20 years its courses of lectures, its assistance to scientific applications in agriculture, its gradual assembling of specialized books and apparatus in a center where no such collections existed before had gone steadily on. Unhappily this progress was to be checked.

Dr. James Apjohn, an M.D. of Dublin University, succeeded Edmund Davy as professor of chemistry in 1826, and one of the last duties performed by Davy in his capacity as secretary was to draw up a letter to His Majesty's Commissioners of Inquiry into the state of education in Ireland requesting that this body should "inquire into and report upon the state of the Royal Cork Institution."[29]

This document set the bell tolling for the institution. Apjohn's tenure of the professorship was short, and a month after his successor, a local medical man, was appointed (July, 1829) the managers of the RCI received a communication from the government inform-

[20] *Phil. Mag.*, **49**, 161–6, 173–8 (1817).

[21] Founded in 1801 by Dr. Milner-Barry, a proprietor of and lecturer in the RCI who did good work for medicine in the city.

[22] *Phil. Mag.*, **50**, 433–7 (1817).

[23] *Ibid.*, **52**, 3–8 (1818).

[24] *Ibid.*, **58**, 241–7 (1821).

[25] *Ibid.*, **54**, 303–6 (1819).

[26] *Ibid.*, **59**, 208–11 (1822).

[27] Introduction to Vol. I, No. I, *The Munster Farmers' Magazine*, Cork, April, 1811.

[28] CLOW, A., AND N. L. CLOW, "The Chemical Revolution," Blatchworth Press, London, 1952, p. 492.

[29] Through Sinclair's exertions the British Board of Agriculture came into being in 1793. The Board arranged for Humphry Davy's lectures on agricultural chemistry in the Royal Institution, London, in 1802.

[29] "RCI Minute Book," p. 10.

ing them that the grant was to be "diminished by one half in 1830 and should cease in 1831."[30]

A study of the minute book in the context of the events of the time suggests that this useful establishment was caught between the upper millstone of bureaucratic absolutism and the nether one of misunderstanding and suspicion, which broadly speaking were the main adverse forces affecting educational developments in nineteenth-century Ireland.

The managers fought a gallant losing battle for the preservation of the institution. Various appeals went to the government and to the public, but the RCI as a teaching and research center declined. Yet the defeat was not a rout. Out of it came a consolidation of public opinion in favor of replacing the institution by an establishment of university status. At first the idea was to have collegiate privileges and the power to grant degrees conferred on the RCI after enlargements of staff and premises. This came to nothing. But after a delay of nearly a decade the work of a body called "The Munster College Committee," a majority of whose members were connected with the institution, bore fruit in the "colleges bill" of Sir Robert Peel, which provided for the establishment of the Queen's University of Ireland with constituent colleges at Cork, Belfast, and Galway. The Cork and Galway colleges are now constituent colleges of the National University of Ireland; that of Belfast has become the Queen's University, Belfast.

[30] "RCI Minute Book," p. 144.

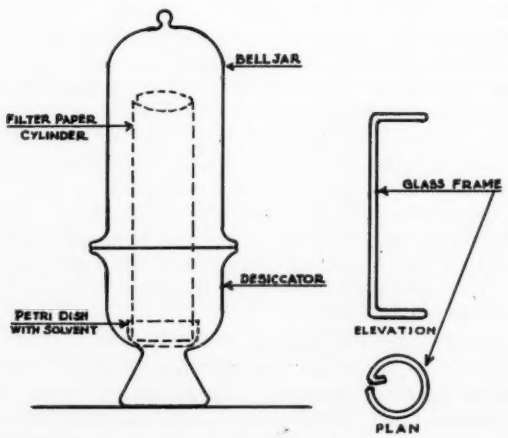
CONCLUSIONS

This account of the RCI has concentrated on its services to science, particularly chemistry. It was also a valuable force in art and archeology. After the establishment of the Queen's college, Cork, in 1849, it continued in its social functions, as a library, and as the headquarters of local scientific and cultural societies. Technical education also benefited by its services. Today its collections are housed in the university and in the Cork Municipal School of Art.

In the changes of the past 120 years the services of Hincks, Davy, and their colleagues to science and to education have been almost forgotten, but the work they so ably and generously inaugurated laid a solid foundation on which the school of chemistry at University College, Cork, has been established. Chemists trained there may well be proud to trace the origins of their school to the work of Edmund Davy. He was a true pioneer of chemical research and education; his achievements and the fact that he was Humphry Davy's assistant during the epoch-making researches in the Royal Institution, London, at the beginning of the nineteenth century will be remembered.

A SETUP FOR TWO-DIMENSIONAL PAPER CHROMATOGRAPHY

E. C. MATHEW and B. M. DAS
Central Leather Research Institute, Madras, India



MOST of the workers who have used paper chromatography as an analytical tool have done it in a suitable cabinet. In spite of the advantages gained by the use of a cabinet, one may not be readily available in an ordinary laboratory. The procedure is rendered still more difficult by the nonavailability of suitable troughs for two-dimensional work. The setup given in the figure surmounts all these difficulties and can be easily prepared. A bell jar (9-in. height), the lower portion of a desiccator (8-in. diameter), and a Petri dish (6-in. diameter) will be enough for filter paper of size 12 in. × 12 in. The filter paper is stitched in the form of a cylinder, the edges not being allowed to touch each other. For thick filter papers like Whatman No. 1 no support is required, while Whatman No. 11 and similar papers need to be supported by a frame made of glass rod, as shown in the figure.

This arrangement was used to study vegetable tannins and was found to work well.

DISTANCE FACTORS IN PAPER CHROMATOGRAPHY

A Senior Project

CONRAD WILLIAM BATT, F.S.C.
LaSalle Academy, Providence, Rhode Island
GEORGE N. KOWKABANY
The Catholic University of America, Washington, D. C.

As an encouragement to promising students, few pedagogical devices are more rewarding than the senior project or thesis.[1] A student, preferably in the senior year, is assigned a problem of some originality in a restricted field of research. The more nearly original the problem, the greater the stimulus to the student's imagination is apt to be. Nevertheless, the limited time available and the student's inexperience require that the experimental techniques used be fairly simple. Also, a more thorough investigation of a somewhat limited aspect of some topic is likely to be more stimulating to the student than a very preliminary attack on a problem of broad import.

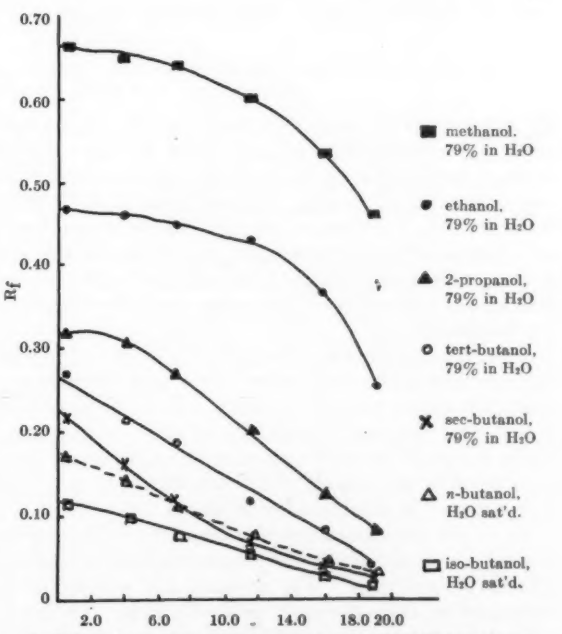
We present here a report on one aspect of a project in paper chromatography which appeared to fulfill the specifications referred to above. The work was performed by a senior student, Brother Conrad William, F.S.C., outside of class hours, for presentation at a regional meeting of the Student Affiliates of the American Chemical Society.[2]

The R_f value, the ratio of the distance a spot has moved on the paper chromatogram relative to the distance the solvent front has moved, depends on a number of factors. Among these is the distance D between the point of initial application of the spot to the paper and the source of developing solvent.[3] It has been shown that the relation between the R_f value and D appears to be approximately linear, R_f values decreasing with increasing D.[4]

The object of the present study was to clarify and extend the relation between the R_f value and the distance of the initial spot from the solvent source.

The solvent developers used were a series of alcohol-water mixtures as shown in the figure. Valine, 0.6 per cent in water, was applied to paper strips with a micropipet. Tapered paper strips, 23.4 cm. long, 3.0 cm. wide at one end, and 2.2 cm. wide at the narrower end, were cut in the machine direction from Whatman No. 1 filter-paper sheets. The strips were mounted in tightly stoppered test tubes, the narrower ends of the strips dipping in the solvent developer. Before development, the strips were "equilibrated" for one hour with the solvent-saturated atmosphere in the test tubes. Using the ascending method, the solvent developer was then allowed to move 22.8 cm. up the strips. Following development the strips were dried and the amino acid was located with ninhydrin. Temperatures during development were not held constant, the runs being made at room temperature. Temperature effects were minimized by making a large number of runs for each determination. R_f values seldom varied by more than 0.01.

The figure shows that the relation between R_f values



D, distance in cm. from solvent source to point of application of spot

R_f Values for Valine/Distance, *D*. Spot is Applied From Solvent Source

[1] Hurd, C. B., J. Chem. Educ. **21**, 81 (1944).

[2] Presented in part and awarded first prize at the regional meeting, Student Affiliates of the American Chemical Society, Notre Dame College, Baltimore, Maryland, April 3, 1954.

[3] Consden, R., A. H. Gordon, and A. J. P. Martin, *Biochem. J. (London)*, **38**, 224 (1944).

[4] Kowkabany, G. N., and H. G. Cassidy, *Anal. Chem.*, **24**, 643 (1952).

and D changes along the series of aqueous alcohol developers from methanol to the butyl alcohols. The relation is approximately linear for the higher alcohols but shows a distinct curvature in the cases of methanol and ethanol. Ignoring the possibilities of adsorption and ion-exchange phenomena, these results may be interpreted in terms of a liquid-liquid distribution process. The amino acid is partitioned between a flowing organic solvent-rich phase containing some water and a stationary cellulose-water complex. The higher alcohols have little tendency to be incorporated in the stationary phase. Thus, the R_f values decline linearly as the flowing phase, moving up the strip, is steadily depleted of water by a kind of "frontal analysis."[4] The behavior of methanol and ethanol, however, supports the hypothesis of Bentley and Whitehead[5] that these alcohols can to some extent compete with water for incorporation into the cellulose phase. In intermediate regions of the R_f/D curves, the incorporation of some alcohol in the cellulose phase forces some water into the flowing phase. Consequently, in these regions R_f values are higher than would be expected. This interpretation implies that the deviation from the type of behavior exhibited by the higher alcohols occurs in the intermediate R_f value range rather than in the lowest.

The decreasing R_f value with increasing D actually appears to depend on the solvent front's being allowed to move a fixed total distance up the strip regardless of the length of D. Preliminary results indicate that if the solvent front is allowed to move the same fixed distance beyond the initial spot, regardless of the length of D, then R_f values become approximately the same for all D's. This is consonant with the idea of a "frontal analysis" of the solvent mixture.

[5] Bentley, H. R., and J. K. Whitehead, *Biochem. J.* (*London*), **46**, 341 (1950).

LOCATION OF THE DECIMAL POINT IN SLIDE-RULE CALCULATIONS

HELEN G. HUSTED
Regis College, Weston, Massachusetts

In the use of the logarithmic slide rule, the usual directions for locating the decimal point by the "digit" method, as supplied by the manufacturers, are cumbersome and time-consuming, and still open to ambiguity. To provide for the needs of science students in the liberal-arts college who have a working knowledge of the use of Briggsian logarithms and how to derive the characteristic of the logarithm of a number, the following rules are presented.

First, a word by way of review. The characteristic for numbers in the units place is zero; and for each successive place to the left of units, the characteristic is 1, 2, 3, etc., up to the total number of such places. Similarly, for each successive place to the right of the decimal point or units place, the characteristic is -1, -2, -3, etc., to the total number of places.

Since for multiplication the logarithmic process is addition, two adjoining one-cycle scales (usually marked C and D) are used. The distance for one factor is measured on D by the appropriate C index. To this is added the distance for the other factor on C by the use of the hairline on the indicator slide. The total distance—*i. e.*, the product—is read at the hairline on the D scale. Now for the decimal point. This depends upon which index of the (movable) C scale is used. If the left-hand index (C_L) is used, the product will have a characteristic which is the sum of the characteristics of the factors, as usual. Thus, for $12 \times 12 = 144$, the characteristic is $1 + 1 = 2$. If, however, the right-hand index (C_R) is used, which is equivalent to using an additional cycle of 10, whose characteristic itself is 1, the final product will have a characteristic equal to the sum of the characteristics of the factors plus an extra 1. Thus: $20 \times 61 = 1220.0$, with a characteristic of $(1 + 1) + 1 = 3$.

For division (subtraction by logarithms) the same two adjoining one-cycle C-D scales are used. From the distance of the numerator measured on D by the indicator hairline, the distance of the denominator on C—also at the hairline—will be subtracted, so that the quotient may be read at either index of the C scale. If the left-hand index C_L is used, the characteristic of the quotient will be that of the numerator minus that of the denominator, as usual. Thus, for $51/17 = 3.0$, the

characteristic is 1 − 1 = 0. If, however, the right-hand index C_R is used, the characteristic of the quotient will be that of the numerator minus that of the denominator, minus an additional 1, to take care of the second cycle of 10. Thus, for 49/7=7.0, the characteristic is (1 − 0)−1=0.

For finding squares or square roots (via logarithms, multiplying or dividing by 2, respectively), the scales must have a 1:2-cycle ratio, and vice versa. Usually these are marked D (1-cycle) and A (2-cycle), both of which are fixed scales. Putting the hairline over the number to be squared on the D scale will simultaneously locate the distance on the A scale which is the square of the original number. If this square falls in the first, or left-hand cycle of A (say A_L), the characteristic is simply 2 times that of the original number. Thus, $(25)^2$ places 25 on D and shows 625.0 on A_L. Hence, the characteristic of the squared number is 2 × 1 = 2. If the square falls in the right-hand or 2d cycle of A (say A_R), the characteristic is 2 times that of the original number, plus 1. Thus, $(45)^2=2025.0$, with a characteristic of (2 × 1) + 1 = 3.

For square roots, a preliminary step is needed. First, the number whose root is wanted is marked off in groups of two as in finding the square root by arithmetic. If a single number is left over, the first cycle of A (A_L) is used; if none, the 2d cycle of A (A_R) is used. By placing the indicator hairline over the square in the correct cycle of A, its square root may be read at the hairline on D. The characteristic of the root depends on which cycle of A is used. If it is the first (A_L), the answer has a characteristic of $^1/_2$ that of the original square; if A_R, the second cycle is used, the characteristic of the root will be (that of the square −1)/2. Examples:

	Groups		*Use*	*Answer on D is*	*Characteristic is*
$\sqrt{625.0}$	6	25	A_L	25.0	2/2 = 1
$\sqrt{6250.0}$	62	50	A_R	79.05	(3 − 1)/2 = 1

For cubes and cube roots, a 1:3-cycle ratio is needed, (usually found in the fixed D-K scales). To cube a number, the hairline is placed on the number in the one-cycle D scale, and its cube is read directly at the hairline on the K scale (3-cycle). If the cube falls in the first cycle of K (say K_L), its characteristic will be 3 times that of the original number. If the cube falls in the middle or second cycle of K (say K_M), the characteristic will be 3 times that of the original number, plus 1. Finally, if the cube falls in the third or right-hand cycle of K (say K_R), the characteristic will be 3 times that of the original number, plus 2. Examples:

$(12)^3$ = 1728.0 in K_L characteristic (3 × 1) = 3
$(35)^3$ = 42,875.0 in K_M characteristic (3 × 1) + 1 = 4
$(63)^3$ = 250,047.0 in K_R characteristic (3 × 1) + 2 = 5

For cube roots a preliminary step is again needed, as in arithmetic. To decide which cycle of K to use, mark off the original cube into groups of three. If there is a single number left over, use K_L (first cycle); if two numbers are left over, use K_M; if three (or none), use K_R (third cycle). Then, if K_L is used, the characteristic of the answer will be that of the cube over 3; if K_M, the characteristic will be that of the cube minus 1, over 3; and if K_R, that of the cube minus 2, over 3. Examples:

	Groups	*Use*	*Characteristic*	*Root*
$\sqrt[3]{6640}$	6640	K_L	3/3 = 1	18.78
$\sqrt[3]{66,400}$	66,400	K_M	(4 − 1)/3 = 1	40.49
$\sqrt[3]{664,000}$	664,000	K_R	(5 − 2)/3 = 1	87.24

For quick reference these rules are given in the table.

Rules For Locating the Decimal Point in Slide-rule Computations

Process	*Cycle ratio*	*Scales usually used*	*Solving conditions*	*Location of decimal point via characteristic of answer*
×	1:1	*C-D*	C_L, left index	Sum of characteristics of factors
			C_R, right index	Sum of characteristics of factors, plus 1
÷	1:1	*D-C*	C_L index	Characteristic of numerator minus characteristic of denominator
			C_R index	Char. numerator minus char. denominator, minus 1
X^2	1:2	*D-A*	Square in A_L	2 times char. original number
			Square in A_R	2 times char. of number, plus 1
$\sqrt{X}$	2:1	*A-D*	Mark off square in groups of 2, 1 no. left over, use A_L	Char. of square over 2
			No nos. over, use A_R	Char. of square minus 1, over 2
X^3	1:3	*D-K*	Cube in K_L	Char. orig. no. times 3
			Cube in K_M	Char. orig. no. times 3, plus 1
			Cube in K_R	Char. orig. no. times 3, plus 2
$\sqrt[3]{X}$	3:1	*K-D*	Mark off cube in groups of 3, one no. over, use K_L	Char. of cube over 3
			2 nos. over, K_M	Char. of cube minus 1, over 3
			No nos. over, K_R	Char. of cube minus 2, over 3

CHEMICAL FURNACES OF ANCIENT MESOPOTAMIA AND PALESTINE

MARTIN LEVEY
Pennsylvania State University,
University Park, Pennsylvania

In order to evaluate the capabilities and limitations of the ancient chemist, it is essential that we be acquainted with his methods of attaining the required heat and necessary temperatures for his chemical processes. That the ancient Mesopotamians and Palestinians attained a marked craftsmanship and extensive chemical technology is known from the artifacts of their civilization. The furnaces used by these early chemists will be described to facilitate our understanding of their technological achievements.

The Mesopotamians, in early times, displayed their respect for the effects of fire by retaining a fire god in their mythology. In the myth of *Sivan*, a Babylonian month, Negun was the fire god. With his assistance fire bricks were made (*1*). The scribes described his name as meaning the fire god who consumes the offerings, "Negun, he that burns by fire" (*2*). The Javelin Star Sirius, which "glows like copper" was identified with Girra the fire god (Sumerian KA+NE) in connection with brick making (*3*). Other fire gods are mentioned in ceremonies of menologies with the *kinūnu*, a brazier dedicated to these gods (*4*). An incantation text of a religious nature preserves the names of two important Sumerian fire gods as BIL·GI and GIŠ-BAR.

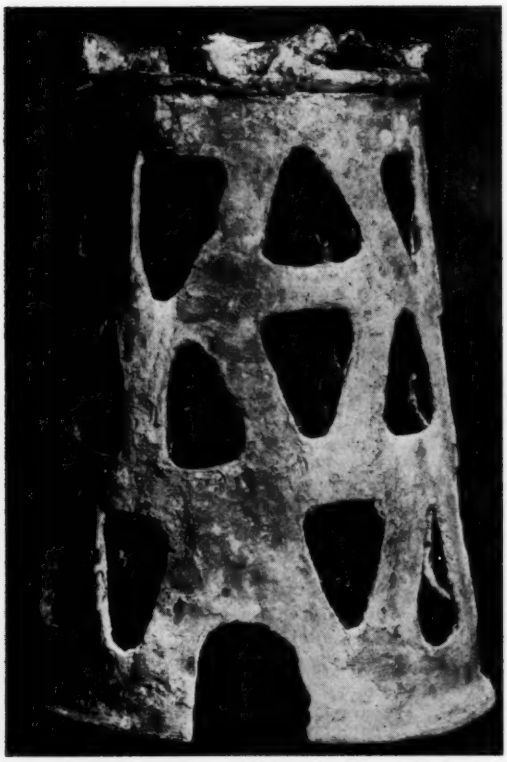


Figure 1. Mesopotamian Furnace of 1400 B.C.

The ancient glass-manufacturing texts and the tablets on perfumery are always careful to denote the intensity of the fire to be maintained. In a tablet on glass manufacture, the text reads (*5*), "Fire is kindled, it may be a good fire, not smoky or a fierce fire, and it rises from the midst of the eyes (the hole openings above the grate)...." In the manufacture of glass and essential oils, the Mesopotamians usually kept the furnace fire going for from four to ten days.

Before opening discussion of the construction of ancient furnaces, it would be of value to determine the types of fuel which were available to the early chemist. As described in the seventh-century B.C. glass texts, decorticated styrax wood or other gummy wood, willow, and perhaps mulberry wood were used. The last of these was cut in the hot month of *Ab* and kept under a hide covering (*6*, *7*). The philological relationship is demonstrated in the early Akkadian, where *abu* signifies firebrand, torch, firewood, while *a-ṕu-u* may mean firewood, rush, fuel (*8*).

For fuel in the 'Arabah of lower Palestine, in the early iron age (second millenium B.C.), there were probably the same supplies that exist today. These consist of dried shrubs and bushes, a very good fuel for the lime-kilns of Palestine and Jordan (*9*). Some wood in the form of charcoal may, however, have been imported into ancient Palestine from Edom proper.

Archeological artifacts have failed to verify the textual evidence for the use of charcoal, mainly because excavators do not always make the significant distinction between accidentally charred wood and prepared charcoal.

At Tell Beit Mirsim, Palestine, in addition to charcoal and wood, dried dung was used. It was not until the latter part of the Middle Ages in our era that the use of dung for this purpose was given up.

The people of Mesopotamia and Palestine possessed a variety of small ovens or stoves of a portable nature. Some of these were designed primarily to keep materials warm. The frontispiece shows a typical example of this

type. This furnace, from the third millenium B.C., is built of clay in the form of a house with the base usually almost square. The lower part is generally divided into two by a wall, while the hind part is two stories high. The two roofs are flat. The knife-cut openings in the shape of triangles, rectangles, or squares are made slightly decorative. The height may range from 70 to 95 cm.

A more common type of furnace is that represented in Figure 1. In this example, from Nuzi, northern Mesopotamia, of approximately 1400 B.C., one may see the draft holes as well as the cutout on the bottom for the introduction of fuel. The round top is evidently for the round-bottomed pots which were prevalent for many heating purposes. This furnace type goes back to at least the fourth millenium B.C. in Assur (*10*). Similar furnaces were in use in prehistoric Europe at a much later date (*11*).

A further development of this furnace is shown in Figure 2, taken from a Mesopotamian seal representation, where the round-bottomed vessel rests on a base exactly like that used by the Arabs in much later times and called by them the *mustauqad* (*12*). No doubt, this was the kind of furnace in use for the distillation and purification of essential oils and for other perfumery operations in which a mild fire lasting for from four to ten days would be required. Charcoal was probably the common fuel used in these furnaces. In none of the small furnaces has there been any evidence pointing to the fact that they may have been grated as we understand the term today. The stokehole was generally designed to act as an air inlet also.

Kilns and large furnaces were well known in prehistoric Sumerian and later times. These may be considered as the progenitors of our modern furnaces.

A very interesting construction is depicted in a prehistoric seal from Susa in Figure 3. On the upper half of the seal, men are shown manufacturing pottery. In the lower half, a domed oven is shown. The dome seems to be fairly low to retain a greater amount of heat. The stacks are short signifying that they served only to carry off the products of combustion and not to produce a draft. The moisture from the heated objects passed off through the stack and the upper row of vent holes. It is difficult to tell from the picture whether or not the flame was in contact with the objects. Unfortunately, the internal construction of the furnace does not appear, and so the exact temperature which it was capable of reaching must remain uncertain. However, the appearance of the furnace resembles somewhat the modern brick kiln. Since two rows of openings are present, one above the other, it is possible that the furnace may have had a grate. From the little that is known of this furnace, it would appear that the technologists of Susa, before 3000 B.C., were capable of producing temperatures close to 1100°C.

Also from Susa, prior to the second millenium B.C., comes another furnace of a different construction (see Figure 4). It has a circular foundation 176 cm. in diameter. It is pierced by 45 flue holes 8 cm. in diameter

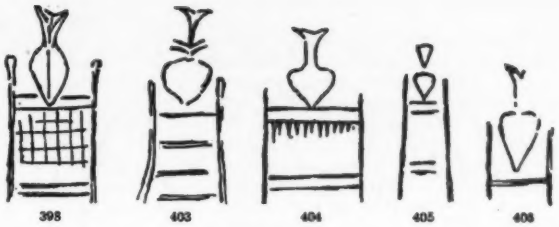


Figure 2. Distillation Furnaces

and has a chimney leading from the fire chamber. The door to the fuel compartment is closed by a stone slab. It is obvious that this furnace could not reach a very high temperature unless some of the flue holes were used as tuyéres to receive blast air from bellows. This is unlikely here since the furnace seems to have been planned for operation at a lower temperature.

A domed furnace has been discovered at Khafaje, in Eastern Palestine, which had been used to burn lime for plaster (*13*). This was demonstrated by analysis of a whitish-gray granular substance found near it containing a large percentage of calcium carbonate. Only the walls were actually found in place. This is understandable since the arch is the weakest part of the furnace, owing partly to pinch spalling (chipping) and

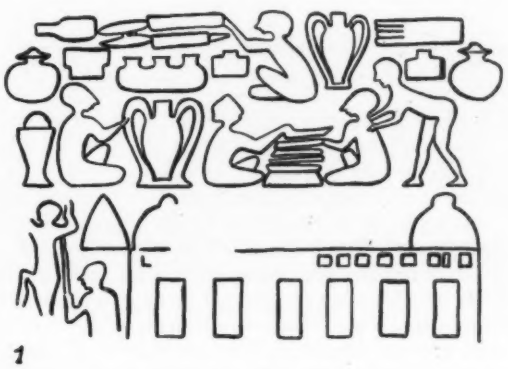


Figure 3. Pottery Making

partly to yielding of the abutments because of the great heat generated. If the temperature goes high enough, the ash which is blown against the roof and sticks to it acts as a flux, causing the roof to melt (*14*).

Domed furnaces (*15*) were widespread in Mesopotamia, with the earliest examples of domed construction going back to the prehistoric Tell Halaf period (*16*). In fact, the beehive-shaped oven is still used near Mosul, Iraq, today.

In glass-manufacturing texts (*17*) which have come down to us there appear to be two distinct types of furnace. The first is the "furnace of the arch (or dome)" (in Akkadian, *kuri ša dakkanni* or *dukkanni*,) described above. Second, there is the "furnace with a floor of eyes" (in Akkadian, *kūri ša šiknat ēnāte meš-sū*). The

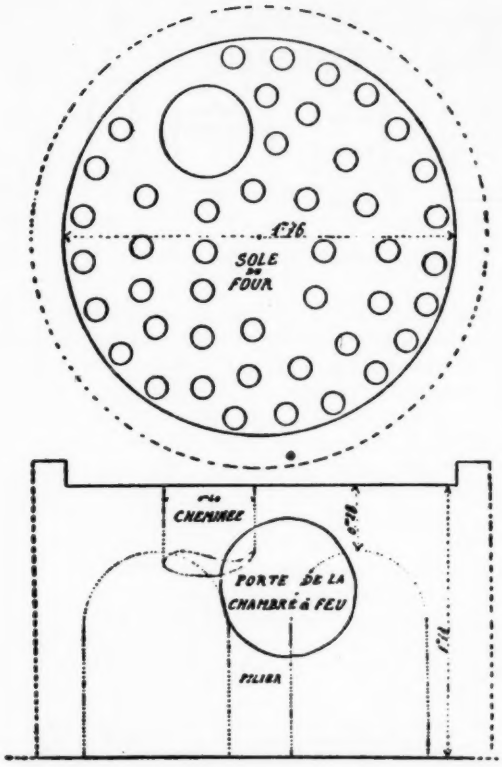


Figure 4. Early Furnace from Susa

"floor of eyes" refers to the perforated level on which the treated objects rest. This furnace, shown in Figure 6, may be used as a kiln or oven, and with the proper roof, for the refining of glass products. If the flames are not entirely returned to the heated objects, then the furnace is probably not so hot and would then be employed for reheating or as an annealing furnace (*18*).

Experimentation with various furnace constructions in the ancient Near East is well demonstrated in the diverse types of furnace in Eastern Palestine. At Kh. el-Jāriyeh, for example, furnaces with circular and rectangular foundations were found (*19*). Some of the smelting furnaces were two stories high, one compartment above the other. This construction is reminiscent of a method of the ancient Chinese of producing high temperatures by placing a series of furnaces on rising ground with common walls (*20*). The bellows were probably used at this site. On this location were found specimens of ore consisting of mixed cuprite and malachite as well as cupriferous sandstone.

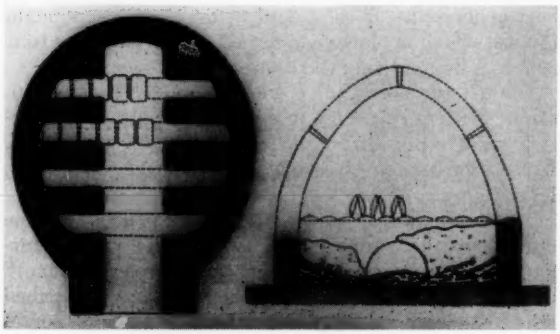


Figure 5. Lime Kiln

The largest and most elaborate copper refinery in the entire ancient Near East was located at Tell el Kheleifeh, at the head of the Gulf of 'Akaba in Palestine. In the tenth century B.C. it was operated by King Solomon, who won it from the Edomites, although it is possible that David first took possession of this town which was first built in the early part of the second millenium B.C. From the remains, it is known that the plants were rebuilt from time to time.

Copper smelting in ancient lower Palestine was probably done at the site of the ore. The smelted copper was then transported to the head of the Gulf of 'Akaba where it was refined. This refining plant was a highly complicated structure whose original walls contained two horizontal rows of flues separated by five rows of bricks. The upper flues led into an air channel extending along the length of the wall. The lower set of flues led into the adjacent room. It is possible that the upper flues were purely for draft purposes while the lower ones allowed gases formed in one chamber to enter and preheat the contents of a second chamber, somewhat on the order of the Chinese furnace mentioned earlier, or on the principle of the modern recuperator.

The refinery was located in a position where it could avail itself of the strong winds which constantly blew from the north down the valley toward the gulf. This steady blast made the use of bellows unnecessary, since the strong drafts of air coming through the flue holes would fan the flames to a great heat. In England, natural draft was early applied to the smelting of such metals as lead. In the north of England the "boles" or "bayle mills," as the furnaces were called, were generally placed on high ground facing the wind (*21*).

The fuel used was charcoal obtained in part from palm wood in the vicinity and the remainder from the woods of Edom. The charcoal was packed about the pottery crucibles which contained the smelted copper. It is believed that the furnace rooms were not roofed (*22*). It is certain that the builders of the copper refinery at Tell el Kheleifeh had had long experience in the metallurgical arts in order to erect such an extensive and intricate plant.

It is regrettable that it is impossible to furnish all details about the furnaces discussed. This is because of the inadequacy of the ancient representations and the destruction, for a variety of reasons, of the furnace remains of antiquity. The literature provides us with very little assistance in our effort to learn the ancient heating methods. In spite of these difficulties, it is clear that the people of Mesopotamia and Palestine possessed portable furnaces and also large ones. The domed furnace was well recognized in antiquity for its ability to achieve higher temperatures; it was probably

the ancient ancestor of our present-day reverberatory furnace. Although chimneys were employed, it is doubtful that their draft powers were fully understood. They were primarily used to remove the fuel-combustion products and waste gases arising from reactions in the furnace hearth. The use of natural draft was brought to a high order of perfection in the refining of copper about 1000 B.C. There is no conclusive evidence for self-feeding furnaces or the grated hearth in antiquity.

With the use of charcoal and the reverberatory or domed furnace having eyes or holes in its upper floor, the highest temperature achieved by the ancient Mesopotamians and Palestinians was probably about 1100–1200°C. This enabled them to carry out the important chemical processes of the melting and refining of metals, manufacture of glass and ceramic products, coking of coal, distillation of zinc and essential oils, and innumerable other operations.

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Figure 6. Furnace with the Floor of Eyes

INSERTING BULBS IN THE VICTOR MEYER APPARATUS

JEREMIAH J. IANNUCCI AND NORBERT ISENBERG

Skidmore College, Saratoga Springs, New York

WHEN the bulbs are lowered into the inner tube of the Victor Meyer apparatus they frequently break because it is difficult to hold them properly. A simple way to lower the bulbs safely is to bend the stem after sealing to form a little hook. The bulbs can then be lowered with a thread.

THE EXAMINATIONS PROGRAM OF THE DIVISION OF CHEMICAL EDUCATION

A Committee Report for the Period 1947–54[1]

THEO. A. ASHFORD, CHAIRMAN[2]
St. Louis University, St. Louis, Missouri

SINCE the last report, given to the Division at the New York Meeting of September, 1947 (*1*), the examinations program has continued with vigor and has further expanded in volume, activity, and scope. The program had been in operation since 1933. The rapid growth of the prewar years was followed by dwindling activity during the war years, and a spectacular upsurge immediately following the war. These were the days when the returning service men were flooding the classes and many chemistry teachers, some of them new in the profession, turned to the tests for ideas and independent evaluation of their performance. Table 1 gives a summary of the activity in terms of sales.

TABLE 1
Test Booklets Sold

1936	10,564	1946	2,095
1937	25,208	1947	55,822
1938	24,100	1948	62,649
1939	25,947	1949	47,972
1940	25,722	1950	35,950
1941	25,750	1951	24,175
1942	21,486	1952	27,350
1943	5,249	1953	26,825
1944	7,878	1954	30,900
1945	4,535		

While the program was in a healthy state educationally, financially it was in a precarious position. It will be remembered that the program has been subsidized from the very beginning. The initial support came from the General Education Fund through the Cooperative Test Service. This agency allocated the necessary funds to Dr. Otto M. Smith, the first chairman of the committee, who, with the guidance of Dr. Ralph Tyler, initiated the construction of these tests. At the same time the Service undertook to provide technical advice to the committee to carry out the necessary statistical studies to publish, and to distribute the tests. However, at no time was the income equal to the expenditures.

In 1947 the Cooperative Test Service was incorporated into the Educational Testing Service. For some time the arrangements with the committee continued on the same basis as before. However, it soon became clear to the E.T.S that the program was costly in comparison with tests in other areas. Moreover, for policy reasons of their own, the E.T.S. was concentrating on tests of general nature, on the high-school and junior-college levels, and in the areas of general education. Specialized courses and professional courses were to be left to other agencies or to the professional societies themselves. Consequently E.T.S. was seeking a way out.

Meanwhile the usefulness of the tests had been established, and the committee was operating at a high level of activity. In any given year some 300 individuals were directly involved in the construction or validation of these tests. More than 700 teachers in 400 institutions were testing over 50,000 students. Literally hundreds of chemistry teachers and collaborators, by correspondence and by personal contact, urged the committee to continue the program.

The committee decided to attempt to operate the entire program by making use of the facilities of the institutions with which the members of the committee and the collaborators were associated. It was already true that much of the work was carried on in these institutions. St. Louis University offered the committee space and facilities. It put at the disposal of the committee the use of the mailing room for advertising and shipping, the tabulating department for records and mailing tests, the testing bureau for analyses and statistical studies, and the comptrollers office for billing and collections. It did this at no overhead charge, but only for the actual extra labor or materials needed for these services. The committee accepted the offer and the program was transferred to St. Louis in April of 1951.

It must be pointed out, however, that St. Louis University does not carry all the burden of the program, though at present it carries the greater part of it. In every school in which the subcommittee chairman is

[1] Reported to the Division of Chemical Education at the 126th Meeting of the American Chemical Society, New York, September, 1954.

[2] The 1953–54 membership of the committee is as follows: L. R. Brantley, Occidental College; S. S. Cooper, St. Louis University; O. C. Dermer, Oklahoma A. & M. College; E. L. Haenisch, Wabash College; F. D. Martin, Purdue University; G. H. Pritham, Pennsylvania State University; C. E. Ronneberg, Denison University; O. M. Smith, Oklahoma A. & M. College; R. L. Van Peursem, Rochester Inst. of Technology; D. D. Wright, Brooklyn College; B. A. Nelson, Wheaton College.

located, work on the construction of tests is being done. It involves correspondence, typing of items, mimeographing, assembling, and mailing. To a lesser extent most schools of the collaborators also contribute. In addition, the schools provide at least partial support in financing the attendance of the committee members to the A. C. S. meetings. It is very gratifying that the administrations of the various schools uniformly consider these professional activities worth while, and encourage their faculty members to participate in them.

The experience we have had since 1951 demonstrates that under the present method of operation the committee can continue to function and still retain the educational values. The committee and the subcommittees have continued to hold conferences, to carry out studies, to construct new tests as needed, and to make them available to each other and to the profession generally. The committee can continue at the present or slightly increased level indefinitely, operating within the income from the sale of the tests, understanding of course that the various institutions will continue to support the committee.

However, the full potentialities of the committee cannot be realized until additional support is found. Much work lies ahead in exploring new activities, devising new techniques of testing abilities and achievements not now tested. Other areas in which these tests can be used wait to be developed. The committee is working to secure help from foundations and industry.

PRESENT STATUS OF THE PROGRAM

Since its inception the committee has constructed 40 tests, including five constructed for the United States Armed Forces Institute. Two or more forms have been constructed in each of six fields of undergraduate chemistry. In the 1953–54 program, 18 different tests were available: general chemistry, four forms; qualitative analysis, four forms; quantitative analysis, three forms; organic chemistry, three forms; physical chemistry, one form; and biochemistry, three forms.

The availability of several forms in each field permits great flexibility. An instructor may select the test that comes closest to the teaching in his class. Where the tests are parallel, or by equating the scores with the aid of the norms, he may use different forms in classes taking the test at different times of the day. He may even use two or more forms in the same class, thus reducing the possibility of cheating. He may use one form as a pretest and the other for a final. The very existence of several forms discourages cramming or attempts on the part of students to obtain a copy of the test before the examination.

The extent of the use of the tests is given in Table 2. Of the 1100 four-year colleges and universities, 452 used the tests in quantity. If to this we add the 68 different schools that ordered specimen sets, we see that nearly half of the institutions teaching chemistry have had direct use of the tests in this period. Similarly, 48 of the 575 junior colleges in the United States used the tests. It is interesting to note that the number of junior colleges participating is increasing. It might also be added that the program increased in volume by about 14 per cent this year over last year.

TABLE 2
Institutions Using the Tests in 1953–54

	Administering test in quantity	*Specimen sets only (additional)*	*Total*
4-yr. colleges and univs.	410	72	482
Junior colleges	42	6	48
High schools[a]	3	11	14
Foreign countries	9	6	15
Industry	5	7	12
Others	2	5	7
	471	107	578

[a] In addition to Ford Foundation study in which eight high schools and eleven colleges participated.

It is more difficult to estimate the number of students tested. Table 3 shows the total sales of answer sheets and test booklets. The total number of students covered by either test booklets or answer sheets is 48,185. The actual number tested must be much larger than this, owing to the practice, encouraged by the committee, that these tests be used repeatedly. Further, some institutions omit some items and often for this and other reasons do not use the special answer sheets. A fair estimate would be that somewhere between 60,000 and 75,000 used the test this year.

Quite impressive is the number of individuals actually involved as collaborators. In the 18 tests featured in the 1953–54 program, the total membership in the subcommittees is 411 from 370 institutions, or an average of 23 persons per test. While there is some duplication in the sense that some individuals participated in the construction of more than one test, the number of *different* individuals as actual members of a subcommittee is 310.

However, the number *collaborating* is considerably larger than this. Some individuals send in items, others criticize the items, still others criticize the experimental forms, or administer the experimental forms in their classes. A fairly large number take the time to report the scores of their students for the calculation of the norms.

Some idea of the number involved in a single test may be exemplified by the following data for general chemistry, Form G. There were 38 individuals as active members of the subcommittee; 12 more submitted items; six additional individuals participated in admin-

TABLE 3
Total Number of Students Tested in 1953–54

	Tests	*Answer sheets*
General	17,025	28,825
Qualitative analysis	4,725	6,750
Quantitative analysis	3,000	5,600
Organic	3,175	4,875
Physical	800	1,350
Biochemistry	2,175	2,975
	30,900	47,375

istering the experimental forms; 30 more acted as reviewers or critics; and 75 reported the success of their students for the calculation of the norms. Thus, no fewer than 160 different individuals participated, some in more than one way, in the construction and validation of this one test.

Analysis of the geographical distribution of the sales shows that the tests were used in every state in the union. They are used roughly in proportion to the number of students in the various sections of the country. Increasing use has been observed on the west coast. In this connection it may be mentioned that a subcommittee has been established in the west-coast area under Dr. Reed Brantley, in California. This subcommittee is currently engaged in obtaining local norms for the California schools.

Of particular interest is the increasing use of the tests in foreign countries. More than 1100 tests have been used in 24 institutions distributed in the following foreign countries: Brazil, Canada, Costa Rica, Cuba, Denmark, Egypt, Hawaii, India, Indonesia, Japan, Lebanon, Nova Scotia, Philippines, Puerto Rico, and Yugoslavia.

This gives the committee an international flavor. Often in quaint English, chemistry teachers from 16 foreign lands wrote either to purchase the tests or to obtain specimen sets to see what chemistry is taught in American colleges. Two different individuals requested permission to translate the tests into Spanish and Portuguese, respectively.

The use of these tests has extended to three more areas. In the past two years more than 30 institutions have used the test for placement of graduate students and for advice on, in what field of chemistry they need review or further study. There have been several requests from industries and government agencies. In this case they are used for quick evaluation of the backgrounds of applicants, or in connection with seminar and refresher courses in the industry.

It is also significant that a number of high-school teachers obtain specimen sets to help them in guiding their bright and promising students. In this connection it may be mentioned that the test was used last year in the Ford Foundation study in which 11 colleges and many high schools participated.

EDUCATIONAL VALUE OF THE PROGRAM

No amount of statistics can give an adequate idea of the educational value of the program. The committee conceives of its function as primarily educational and its concern about finances or size, as a necessary prerequisite to achieving the educational objectives.

The greatest value is derived by those actively engaged in the construction of the tests. It gives the opportunity for diverse individuals, with widely different backgrounds, points of view, temperaments and experiences, to meet with one another and consider a common problem. The immediate objective—the test to be prepared—serves as the means of bringing them together to exchange ideas and learn from one another. The total resource of the committee is the sum total of all the knowledge and experience of the collaborators.

However, the consideration of test items is not merely an artificial device. Testing is central to teaching. When the participants debate what is important to test, they are really debating what is important to teach. Disagreements naturally arise. In defending their points of view, the participants get a clearer notion of what they should teach and why. Indefensible points of view give way. More advanced points of view are adopted. Sometimes compromises have to be made. No one individual is always right, particularly if he had never thought much about an issue. In this intensive give and take everyone profits and everyone contributes. Even misconceptions about factual or scientific matters are cleared up. The participants grow professionally and the teaching of chemistry gains. Even if no test were constructed, the value received in these conferences alone is worth the activity.

Nor are the contacts limited to those attending the meeting. A good deal of the work is done by correspondence and thus, vicariously, chemistry teachers get acquainted with other teachers throughout the nation. No other activity brings together so many teachers to argue so intensely on so many specific issues.

Many of these educational values flow out into the users. Once the tests are constructed they are available to the entire teaching profession.[3] They contain ideas and suggestions of what others consider important to test and to teach. They set the pace for better teaching and point the way to the future. They permit comparisons of performance with different schools or, within the same school, between classes and from year to year.

A by-product of this activity is that of the studies that are carried out by the committee. Before constructing a test each subcommittee surveys the field to discover what tests are used, length of courses, time devoted to each area, the emphasis placed on major topics, and the like. These surveys are widely circulated and often published (*2–7*).

The existence of valid and reliable tests[4] in this area also stimulates educational study and experimentation. Whenever an experiment is carried out, the results must be measured by valid means. The use of these tests has already been mentioned in the Ford Foundation study (*8*). Other studies have been reported in THIS JOURNAL (*9*) and in master's and doctor's theses.

When the test emerges in the final form, after two years of discussion, criticism, and experimental trial, it represents the combined wisdom of a hundred or more individuals. It possesses a high validity. It contains the combined judgment of what is important to teach and common to a great variety of courses, as actually given throughout the nation. Likewise, it possesses a high degree of reliability since every item is pretested

[3] The tests may be obtained from the Examinations Committee, A. C. S., St. Louis University, St. Louis 4, Missouri.

[4] These tests are critically reviewed in the "Mental Measurement Yearbook," O. K. Buros, Editor, Rutgers University Press, New Brunswick.

and statistically analyzed. An item is not included in the test unless it helps distinguish between good and poor students.

The strength of the test also is in part its weakness. Any given test is not perfectly appropriate for any given course. Courses vary from school to school that the varying needs of a given school or class may be met. They also should vary in order to encourage experimentation. Equally important is the fact that every teacher is unique. He has some excellence in one respect or another which is not shared by the majority of teachers. From the very process of the construction, the test cannot and does not test these unique features of a course.

However, all this merely argues that the test should be used for what it attempts to do and no more. It does measure accurately, quickly, and reliably a great number of ideas, all of them important and common to the vast majority of courses. In any given course the unique elements should be tested by an additional, perhaps short test.

With all these limitations it is still true that the tests measure a large fraction of the important outcomes common to most courses. They cannot do the whole job of evaluating, but what they do, they do effectively and reliably. This frees the teacher to concentrate on the less easily evaluated outcomes. Moreover, on the basic material they permit the teacher to compare himself with others in his school or the schools of the nation.

One of the important values of the test is that it provides national norms that permit comparisons. The norms are calculated by taking an adequate sample of all who have given the test and have sent in the reports of the scores of the students. In all cases, except in the tests used for the first time, the norms are sent with the tests so that the teacher can make immediate comparisons. In most instances the norms are reported in THIS JOURNAL for ready reference (*10–17*). In the new tests, the norms are mailed to the users as soon as they are calculated.

The committee has found that the norms are remarkably stable from year to year. Thus, the norms calculated for general G in the basis of returns of 25 institutions in 1953 were practically identical with the norms based on the 1952 program and from 38 mostly different institutions. Nevertheless, the committee continues to calculate newer norms if the reports sent in contain a sufficient number of cases.

ACKNOWLEDGMENT

The author wishes to express his debt to the members of the committee, the chairmen of the subcommittees, the members of the subcommittees, and to the larger group of collaborators. It is these men who have given generously of their time, effort, and personal expense, who are responsible for the work reported here. They have developed instruments and powerful tools for the improvement of chemistry teaching.

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A MNEMONIC FOR DICARBOXYLIC ACIDS

GERALD J. COX
University of Pittsburgh, Pittsburgh, Pennsylvania

THE mnemonic of DeLoach and Brandon for the aldoses[1] recalls one long remembered for the dicarboxylic acids. "Omsgapsas" gives the first letter of oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azaleic and sebacic acids.

[1] J. CHEM. EDUC., **32**, 136 (1955).

SIMPLE APPARATUS FOR REFRIGERATION EXPERIMENTS

M. A. GOVINDA RAU[1] **and M. G. SUBBA RAU**
University of Madras, Madras, India

THE usual equipment commercially available for refrigeration experiments of one-half ton or more capacity, and generally using ammonia as a refrigerant, are rather elaborate and costly. A simple piece of equipment can easily be set up in any engineering laboratory, using the ordinary, readily available household Freon refrigeration units of about one-fourth ton capacity. The detachable evaporator coil is mounted inside a coil of three-quarter-inch copper tube forming a double-tube heat exchanger system. The usual air-cooled condenser in such a unit is similarly replaced by another double-coil spiral heat exchanger.

With the unit used in our chemical engineering laboratory, each coil had 10 turns of 18-inch diameter, making the total length of the tube about 50 feet. The evaporator coil was completely lagged and embedded inside a cylindrical wall (3 inches thick) of lagging of asbestos magnesia, and painted over with aluminum. The condenser coil was only painted with aluminum. Water from a constant-level overhead tank was passed through the two coils so that the discharge from the evaporator coil was cooled and that from the condenser coil heated up. It is simple to determine the heat absorbed in one and rejected in the other. From the usual pressure gages supplied with such equipment, all necessary data for calculating the c.o.p. (coefficient of performance) can be obtained. An energy meter in the electrical mains gives a measure of the actual power consumed and thus the actual c.o.p. in the system can be calculated.

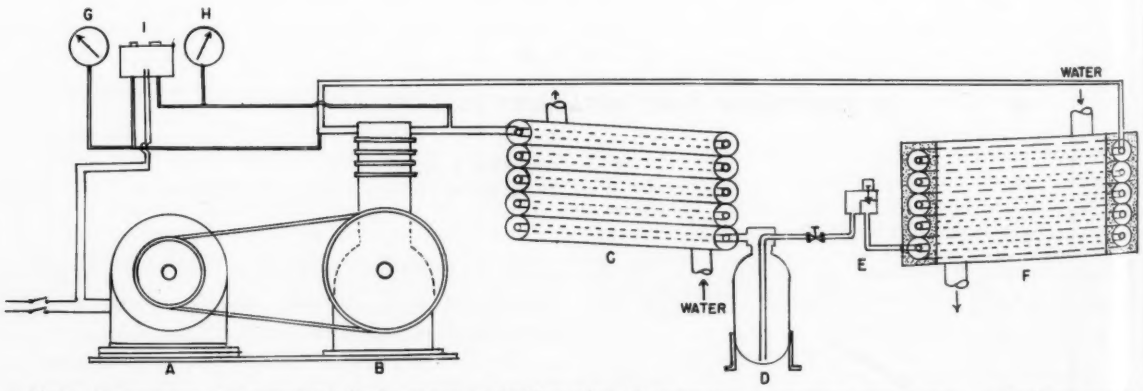
It is obvious that the same experiment can also be used to illustrate the working of a heat pump. In this case, heat is pumped from one stream of water to another, making the former cold and the latter hot. Indeed, since both streams come from the same source, the experiment illustrates a method of pumping heat from one part of the liquid to another. The efficiency of this heat pump can be evaluated from the same data, as shown in the calculations.

A specimen set of data obtained with this equipment is given below.

Refrigerant used: Freon 12. (Thermodynamic data for Freon 12 taken from Perry, "Chemical Engineers Handbook," 3rd Edition, 1951, p. 261.)

(1) Condenser pressure: 130 p.s.i.g.
(2) Evaporator pressure: 26 p.s.i.g.
(3) Heat absorbed in evaporator:
  (*a*) Inlet temperature of water: 89°F.
  (*b*) Outlet temperature of water: 71°F.
  (*c*) Rate of water flow: 202 lbs./hr.
  (*d*) Heat absorbed: $202.5 \times 1 \times (89-71)$ = 3645 B.t.u./hr.
(4) Heat rejected in condenser:
  (*a*) Inlet temperature: 89°F.
  (*b*) Outlet temperature: 97°F.
  (*c*) Rate of flow of water: 495 lbs./hr.
  (*d*) Heat rejected: $495 \times 1 \times (97-89)$ = 3960 B.t.u./hr.

[1] EDITOR'S NOTE: We regret to note that one of the authors of this paper, Dr. M. A. Govinda Rau, died suddenly in November of last year, after this manuscript was submitted.



A, Motor; *B*, compressor; *C*, condenser; *D*, liquid receiver; *E*, throttling valve; *F*, evaporator; *G*, evaporator pressure gage; *H*, condenser pressure gage; *I*, pressure switch (Pressostat).

(5) Power consumed: 0.533 kw.-hr./hr.
1820 B.t.u./hr.

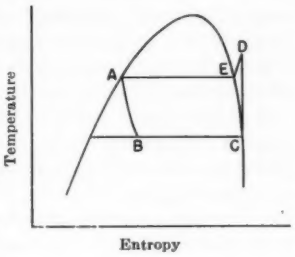
REFRIGERATION CALCULATIONS

Heat absorbed/lb. of Freon
$= H_C - H_B$
$= H_C - H_A$
$= 81.28 - 33.65$
$= 47.63$ B.t.u.

Mechanical work done/lb. of Freon (assuming adiabatic compression of dry saturated vapor from C)
$= H_D - H_C$
$= 90.25 - 81.28$
$= 8.97$ B.t.u.

Theoretical c.o.p. $= \dfrac{H_C - H_B}{H_D - H_C} = \dfrac{47.63}{8.97} = 5.3$

Actual c.o.p. $= \dfrac{\text{heat absorbed in evaporator}}{\text{work done}} = \dfrac{3645}{1820} = 2.0$



Relative c.o.p. (actual/theoretical) $= \dfrac{2}{5.3} = 38\%$

HEAT-PUMP CALCULATIONS

Heat delivered/lb. of Freon $= H_D - H_A$
$= 90.25 - 33.65$
$= 56.60$ B.t.u.

Mechanical work done/lb. of Freon (assuming adiabatic compression of dry saturated vapor from C)
$= H_D - H_C$
$= 90.25 - 81.28$
$= 8.97$ B.t.u.

Theoretical c.o.p. $= \dfrac{H_D - H_A}{H_D - H_C} = \dfrac{56.60}{8.97} = 6.32$

Actual c.o.p. $= \dfrac{\text{heat delivered in condenser}}{\text{work done}} = \dfrac{3960}{1820} = 2.175$

Relative c.o.p. = actual/theoretical
$= \dfrac{2.175}{6.32} = 34.4\%$

Besides providing a simple quantitative experiment, this apparatus allows the students to get acquainted with the automatic pressure controls and throttle adjustment which are supplied with such units.

SYNTHESIS OF COPPER (I) SULFIDE

SAMUEL R. SCHOLES, JR.
Alfred University, Alfred, New York

MANY laboratory texts used in college general chemistry courses present the synthesis of copper (I) sulfide as an early experiment to demonstrate the quantitative aspects of compound formation. Almost all the procedures suggest that the synthesis be performed by heating the elements in a covered porcelain crucible from which the excess sulfur is distilled and burned under a good hood. As some laboratories have not sufficient hood space to permit this preparation to be accomplished by an entire class, it is suggested that the formation of sulfur dioxide fumes be avoided by a small-scale procedure.

Place the copper wire in a porcelain combustion boat. Cover the wire with powdered sulfur and insert the boat to the bottom of a Pyrex test tube which is clamped in a nearly horizontal position, but inclined so that the mouth of the tube is lower than its closed end. The mouth of the tube is closed by a loose plug of glass wool, and the end near the boat is heated. The excess sulfur condenses on the cooler part of the tube. After the excess sulfur has been distilled from the boat, the tube near the boat is heated strongly before it is allowed to cool to room temperature. To conclude the experiment, the boat and its contents are removed from the tube and weighed.

Using 0.2- to 0.4-gram samples of No. 24 copper wire, a 60-mm. porcelain combustion boat in a 150- × 16-mm. Pyrex test tube, and performing all weighings to the nearest milligram, students obtained a mean value of 20.6 per cent sulfur in the compound. This compares satisfactorily with the theoretical value of 20.1 per cent sulfur in copper (I) sulfide.

THE VAN DER WAALS GAS EQUATION

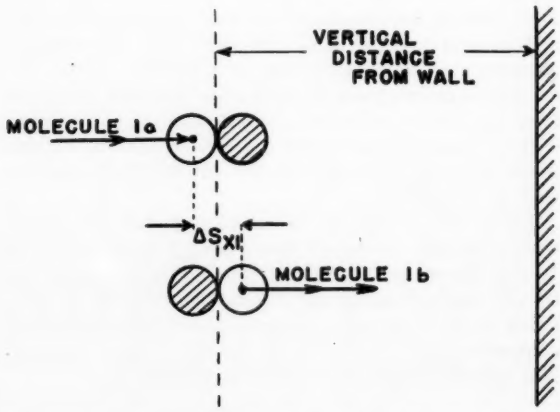
A Simple Kinetic Treatment

ELLICE S. SWINBOURNE
New South Wales University of Technology,
Sydney, Australia

THE van der Waals gas equation is of particular interest to lecturers in the field of physical chemistry, because it provides the undergraduate with an excellent example of a relationship derived from an ideal system which has been modified to satisfy real conditions. The literature is full of more exact and more elaborate equations of state (*1*), but the special appeal of the equation of van der Waals lies first in the simple nature of the two correction terms, and second in the ease with which it may be handled mathematically. While students may readily appreciate the need for these two correction terms, it is the experience of the author that they rarely understand the true significance of the terms or the manner of introduction into the ideal equation of state. Most of the less elaborate treatments presented in texts are vague and frequently incorrect, while those of a more mathematically elegant nature (*2*, *3*) are invariably far too complicated to be readily assimilated by the undergraduate. There is an evident need for justification of the equation in terms of a simple but nevertheless physically accurate picture.

THE VAN DER WAALS CORRECTION TERMS

By ways of review: The ideal gas law ($PV = RT$) may be obtained by the application of the laws of classical mechanics to a system consisting of a dispersed assembly of hard spheres (representing the molecules) which move about in a random manner inside a container. It is assumed that the volume of each sphere is negligibly small compared with the average free space available for it to move about in, and that there are no forces of attraction or repulsion between the spheres, all collisions being instantaneous.



Two Pairs of Molecules Colliding Simultaneously at Equal Distances from Wall *X*

Van der Waals modified the ideal equation in the following manner (*4*, *5*, *6*): He subtracted a constant b from the total volume of the system to allow for the volume occupied by the molecules, and he added a term a/V^2 to the pressure in order to take into account errors occasioned by neglecting the presence of molecular forces (a/V^2 is called the "internal pressure" or sometimes the "cohesive pressure"). This new equation, $(P + a/V^2)(V - b) = RT$, quantitatively predicted the behavior of real gases under conditions of moderate temperature and pressure, and at least qualitatively under conditions approaching the critical point, but van der Waals' reasoning was for many years a subject of much controversy.[1] In the words of J. S. Haldane (*8*), "Doubt seems to have been stifled by the remarkable practical success of the equation. It was also a fascinating mathematical plaything."

It can be demonstrated that the two correction terms may be explained by the use of simple modifications to the kinetic picture which is commonly used for the students' proof of the ideal gas law. The approach to the problem is not original (see for example later references) but does not appear to be in common use.

EXAMINATION OF THE KINETIC PICTURE OF THE IDEAL GAS

A cubic container of side s may conveniently be assumed to house the dispersed assembly of randomly moving spheres previously referred to, the gas pressure being identified with the rate of change of momentum of the spheres as they strike unit area of any face. Thus, in order to calculate the contribution that molecule No. 1 makes to the pressure on two opposing faces, X and X', the molecule is treated as moving with a numerically constant component momentum $\pm mu_{1x}$ (considered perpendicular to the faces) backward and forward between the two walls. Molecule No. 1, however, in its travel must suffer frequent collisions with other

[1] Note J. C. Maxwell's comments (*7*) and also the famous triangular argument among Lord Rayleigh, P. G. Tait, and D. T. Korteweg in *Nature*, **44**, 499, 546, 597, 627 (1891); **45**, 80, 152, 199, 277 (1892).

gas molecules and it therefore undergoes *frequent changes* in momentum. At first sight, then, the treatment assuming constancy of momentum appears to be an unreal one; nevertheless, the following explanation should serve to justify the assumption.

The momentum mu_{1X} is really a representative of the universe of momenta being transported between the two walls. Although the individual molecules may undergo frequent changes in momentum, the *statistical distribution* of these momenta does not change. If attention is confined to collisions in a thin wafer of gas parallel to the walls X and X', then it can be observed that in order to maintain an unaltered distribution, for every molecule with momentum mu_{1X} entering into a collision and suffering a consequent change in momentum, there must be at the same instant an equal likelihood of another molecule's emerging with momentum mu_{1X} from another collision. Thus, in following the transport of this momentum from wall X' to X, it is necessary to shift attention constantly from one pair of molecules undergoing a collision to another pair also undergoing a collision at the same time and at the same vertical distance from the wall X. The molecule No. 1 with constant momentum $\pm mu_{1X}$ is seen to be a *hypothetical* molecule used to simplify the mathematical argument.

The time between successive strikes on wall X is $2s/u_{1X}$ and the change in momentum for every such strike equals $2mu_{1X}$. Therefore:

$$P_{1X} = \frac{mu_{1X}^2}{s^3}$$

Summing for all molecules,

$$P = \frac{nmu_{RX}^2}{V}$$

$$PV = {}^1/_3\, nmu_R^2$$

Identification of the mean molecular kinetic energy ($^1/_2\, mu_R^2$) with the absolute temperature, leads to the ideal gas relationship,

$$PV = RT \text{ per gram molecule}$$

CORRECTION FOR MOLECULAR VOLUME

The first modification of the above ideal gas picture is to consider the molecules to be of a finite size in comparison with the average available free space. In all other respects the picture remains unchanged.

Examination of the accompanying diagram will indicate a slight inaccuracy in the previous argument concerning *hypothetical* molecule No. 1. In instantly transferring attention from molecule No. 1*a* (undergoing collision) to molecule No. 1*b*, the representative momentum mu_{1X} has actually been advanced a distance Δs_{X1} in zero time. In other words, during a collision the molecular momenta are transported instantaneously over a small finite distance.[2]

The mean value for Δs is the same as that estimated by van der Waals (*10, 11*) for the shortening of the mean free path owing to finite molecular size:

$$\Delta s = \frac{\sqrt{2}\sigma}{3}$$

and:

$$\Delta s_x = \frac{\sqrt{2}\sigma}{6}$$

A number of collisions equal to $2s/L_X$ (*i. e.*, $4s/L$) therefore complicates the travel of the hypothetical molecule between successive strikes on wall X.

Thus, between these strikes, the molecule must be considered as traveling a distance equal to $4s\Delta s_X/L$ in zero time (*i. e.*, a distance equal to $2\sqrt{2}s\sigma/3L$).

The rate of change of momentum for molecule No. 1 on wall X now becomes $mu_{1X}^2/(s - \sqrt{2}\, s\sigma/3L)$.

$$P_{1X} = \frac{mu_{1X}^2}{s^3\left(s - \frac{\sqrt{2}\, s\sigma}{3L}\right)}$$

Assuming Maxwell's formula for the mean free path (*12*), and summing for all molecules:

$$P = \frac{{}^1/_3 nmu_R^2}{s^3\left(1 - \frac{2n\pi\sigma^3}{3s^3}\right)}$$

$$P(V - {}^2/_3 N\pi\sigma^3) = RT \text{ per g. mol.}$$

The form of the van der Waals equation, correcting for molecular volume only, is:

$$P(V - b) = RT$$

Therefore:

$$b = {}^2/_3 N\pi\sigma^3$$

= four times the total molecular volume

Molecular diameters calculated from experimental values for b are found to be in reasonable agreement with those obtained by other methods, *e. g.*, gas viscosity measurements (*13*), X-ray crystal studies (*14*), etc.

CORRECTION FOR INTERMOLECULAR FORCES

Explanations for internal pressure must be considered as unsatisfactory if based on the picture of a cumulative attractive force field from the body of the gas, tending to retard the motion of molecules approaching the sides of the container.[3] This is because such arguments neglect the much more intense attractive force field presented by the wall itself.

Internal pressure can be more correctly interpreted in terms of the chaotic molecular motion at any point *within* the gas by demonstrating that the existence of molecular forces causes the time of collision between real molecules to be greater than for ideal ones.[4]

Two possibilities merit discussion: first, the con-

[2] D. T. Korteweg (*9*) discussed this "economy of time due to molecular collisions" and maintained that in 1877 he had solved the problem for spherical particles in three dimensions.

[3] This kind of reasoning, originally used by van der Waals, is still given by some authors.

[4] This explanation for internal pressure is not new (*15, 16*) and is probably originally due to G. Recknagel (*17, 18*); however, authors do not make clear the *reason* for the time delay during molecular collision.

tinuous formation and dispersion of molecular clusters—this should be important only under conditions near the condensation point (*e. g.*, in nucleation behavior); but there appears to be only one logical explanation to account for internal pressure in gases removed from condensation conditions—that of "soft" binary collisions.

Picture once more the hypothetical molecule No. 1 moving backward and forward between the faces of the cube, assuming that because of force fields it is delayed an amount of time τ in every binary collision. The time between successive strikes on wall X now becomes equal to $2s/u_{1X} + 4s\tau/L$. (Neglect the correction for molecular volume.) Thus:

$$P_{1X} = \frac{mu_{1X}}{s^2\left(\frac{s}{u_{1X}} + \frac{2s\tau}{L}\right)}$$

$$P_{1X}\left(1 + \frac{2u_{1X}\tau}{L}\right) = \frac{mu_{1X}^2}{s^3}$$

Allowing that for the correction term only, $P_{1X} \cong \frac{mu_{1X}^2}{s^3}$, and making use of Maxwell's equation for the mean free path:

$$P_{1X} + \frac{2\sqrt{2}\pi\, nm\sigma^2 u_{1X}{}^3\tau}{s^6} = \frac{mu_{1X}^2}{s^3}$$

For one gram molecule of gas, the relationship approximates to:

$$P + \frac{2\sqrt{2}\pi N^2 m\sigma^2 u_{RX}^3\tau}{3V^2} = \frac{RT}{V}$$

The form of the van der Waals equation correcting for internal pressure only is:

$$P + \frac{a}{V^2} = \frac{RT}{V}$$

Therefore, noting that $^1/_3\, Nmu_R^2 = RT$:

$$a = 2\sqrt{2}\pi\, NRT\sigma^2 u_R\tau \qquad (1)$$

FORCE FIELD AS A CAUSE OF TIME DELAY

In the ideal picture, molecules do not exert forces at a distance and therefore approach each other with constant velocities. At the point of collision these instantly undergo change, the two molecules moving apart with altered velocities, which however remain constant at their new values. On the other hand, real gas molecules in their movement through space continually exert forces upon each other which are of negligibly small magnitude except during close molecular encounter, when they become considerable. Thus, for a real system the respective velocities during the approach and departure of two colliding molecules are *not* constant, but undergo *continual* change.

Consider for example a head-on collision between two real gas molecules, both moving with numerically identical velocities. If the over-all *velocity of approach* at any time is $2U$:

$$2U = -\frac{dr}{dt}$$

By the law of conservation of energy:

kinetic energy + potential energy at distance r = kinetic energy + potential energy at distance r_o

$$mU^2 + \epsilon_r = mU_o^2 + O$$

$$U = \left(U_o^2 - \frac{\epsilon_r}{m}\right)^{1/2}$$

The time required for the molecules to move from r_o to r is:

$$t = -\int_{r_o}^{r} \frac{dr}{2U}$$

In the ideal case, the velocity is constant at $2U_o$; therefore the *extra* time required (*i. e.*, in excess of the ideal) for the *real* molecules to move from r_o to r is given by:

$$\Delta t\,(r_o \rightarrow r) = -\,^1/_2 \int_{r_o}^{r}\left(\frac{1}{U} - \frac{1}{U_o}\right) dr$$

The real molecules continue to approach each other until the distance of separation is such that the original kinetic energy (in the absence of force fields) is exactly balanced by the intermolecular potential energy—*i. e.*, until $\epsilon_r = mU_o^2$. The extra time taken for a real molecule to arrive at this distance is:

$$\Delta t = -\,^1/_2 \int_{\epsilon_r\,=\,0}^{\epsilon_r\,=\,mU_o^2}\left(\frac{1}{U} - \frac{1}{U_o}\right) dr$$

It follows that the departure from the point of collision involves exactly the same amount of time. That is, the *total* time lost by real molecules during the complete process of the "soft" head-on collision equals $2\Delta t$.

$$2\Delta t = \int_{\epsilon_r\,=\,mU_o^2}^{\epsilon_r\,=\,0}\left[\left(U_o^2 - \frac{\epsilon_r}{m}\right)^{-1/2} - \frac{1}{U_o}\right] dr \qquad (2)$$

(The commonly used relationship (*19*) for ϵ_r is $\epsilon_r = \lambda r^{-12} - \mu r^{-6}$).

In order to estimate correctly the time delay for an *average* collision, it is necessary to consider all angles of approach of the two molecules and all combinations of velocities taken two at a time.[5]

This presents a difficult mathematical problem. For

Comparison Between Values for a (Absolute Units $\times 10^{-12}$), as Estimated from Critical Data and as Calculated from Equations (1) and (3). (Temperature, 0°C.)

Substance	*Critical data*	*Calculated*
He	0.03	0.09
Ne	0.21	0.24
H_2	0.25	0.29
A	1.36	0.38
N_2	1.41	0.49
Kr	2.35	0.44
Xe	4.15	0.58

[5] Compare with the Clausius Virial approach to the problem as adopted by M. Reinganum (*20*).

the purpose of an approximate calculation, however, let it be assumed that the average can be represented by the value of $2\Delta t$ for a head-on collision of the type indicated above, in which $U_o = u_{RX}$. Substitution in Equation (2) gives the result:

$$\tau \cong \frac{\sqrt{3}}{u_R} \int_{\epsilon_r = kT}^{\epsilon_r = 0} \left[\left(1 - \frac{\epsilon_r}{kT} \right)^{-1/2} - 1 \right] dr \qquad (3)$$

Although this integral cannot be solved analytically a numerical solution can be obtained[6] using known values for λ, μ (*21*, *22*, *23*) and T. On this basis, and by the use of equation (1), values for the van der Waals constant a have been calculated for gases at a temperature of 0°C. (See the table.) Considering the assumptions made, the agreement with a as estimated from critical data[7] is reasonable, deviation being greatest for the higher molecular weight gases. In this regard some of the difficulty appears to lie with the choice of satisfactory values for the collision diameters (the values taken are those estimated from gas viscosity measurements (*26*). Also, the frequency of collision between attracting spheres would be greater than that calculated on the basis of the rigid sphere model used to estimate a in terms of τ (see equation (1)).

It is perhaps interesting to note that while this kinetic treatment accounts for the internal pressure of gases in terms of the "softness" of the intermolecular *repulsive* forces, the normal thermodynamic approach accounts for the same phenomenon in terms of the strength of the *cohesive forces.*

CONCLUDING COMMENTS

It has been demonstrated that the two van der Waals correction terms can be justified by simple treatment of the kinetic picture of a hypothetical gas molecule moving backward and forward with constant component velocity between opposite faces of a cube. Collisions are shown to complicate the travel of this molecule in two ways.

(1) *Because the molecules have a finite volume, they can interchange momentum without the need for coincidence of their centers, and therefore the transport of momentum between the two faces is faster than in the ideal case.*

(2) *Real molecules do not undergo instantaneous collision, and thus the gain in time mentioned above is diminished by an amount dependent upon the nature of the intermolecular force fields.*

These two factors can be *conveniently* allowed for by the subtraction of a constant b from the volume of the container, and the addition of a term a/V^2 to the pressure exerted by the real gas molecules upon the walls.

The treatment introduces these corrections into the ideal gas equation independently of one another; a more complete picture should take into consideration the *mutual* effect of both. At least in the case of simple molecules there appears to be reasonable dependency of b upon molecular size and of a upon molecular force fields, each taken separately. Nevertheless, considering the oversimplified nature of the approach the search for such agreement should not be pursued too far in the case of more complex molecules.

[6] For the purpose of numerical integration the author found it convenient to change the variable from r to $\left[1 - \left(\frac{\epsilon_r}{kT}\right)^{1/2}\right]^{1/2}$

[7] The values for the van der Waals gas constants as estimated from critical data (*24*) are more readily available but less reliable than those from other sources (*25*).

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance given by L. W. O. Martin, of the N.S.W. University of Technology, during many interesting discussions.

SYMBOLS USED

a,b	van der Waals gas constants
k	Boltzmann gas constant
L	mean free path of the gas molecules
L_X	mean component free path
m	mass of a molecule
M	gram molecular weight
n	total number of gas molecules in the system
N	Avogadro's number
P	over-all gas pressure
P_{1X}	pressure exerted by molecule No. 1 on container walls X and X'
r	distance of separation of two molecules
r_o	r sufficiently large for the intermolecular potential energy to be negligible
R	universal gas constant per gram molecule
s	length of the side of the cubic container holding the gas
t	time
T	absolute temperature
u_1	velocity of molecule No. 1
u_{1X}	component velocity of molecule No. 1 along the x axis
u_R	root mean square velocity of the molecules
u_{RX}	root mean square component velocity along the x axis
U	one-half the velocity of approach of two colliding molecules
U_o	U at distance r_o
V	volume of the container
x	axis perpendicular to opposite faces of the cube, X and X'
σ	collision diameter of the molecules
π	3.1416, etc.
τ	average time delay during a collision between real gas molecules
ϵ_r	the intermolecular potential energy between a pair of molecules r distance apart
λ, μ	molecular constants in the mathematical relationship for ϵ_r

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HOW TO USE RADIOCARBON CHEMICALS IN TEACHING

RICHARD H. ROBINSON[1]
Fisher Scientific Company, Pittsburgh, Pennsylvania

THE recent public availability of safe, low-activity, relatively inexpensive radiocarbon compounds[2] presents a fine opportunity to students and teachers everywhere for a variety of interesting and instructive applications.

After acquiring a few vials of radiocarbons, a counting chamber, and a scaler, what then? It is the purpose of this article to describe for those who have not followed this interesting new field of research very closely, a few representative applications, easily set up in classroom or school laboratory, with the hope of arousing increased interest in the valuable lessons that tracer studies can teach.

THE ISOTOPIC DILUTION METHOD

For the budding biochemical analyst, this technique offers many possibilities for bypassing improbable quantitative chemical determinations of a desired compound in a mixture of similar compounds. It can also be used to shorten many other analytical methods whose only objectional feature is that they take too long.

Figure 1 illustrates the simplicity of the fundamental method. A typical experiment might result in the following data:

B 2000 c. p. m.
C 60 mg.
500 c. p. m.

Then $A = \frac{2000\ (60)}{500} - 40 = 200$ mg. of benzoic acid in the crude mixture, an accurate quantitative determination without a *quantitative* chemical isolation.

To clarify, one might think of the activity added at the beginning of the assay as having similar characteristics to those of a coupling reagent for a colorimetric determination. The activity, considered as a material quantity, mixes intimately with all of the inactive benzoic acid in the crude mixture to give the benzoic acid in the sample a certain *specific* activity in counts per minute per milligram.

Then, if any benzoic acid at all can be isolated, it will have the same *specific* activity in counts per minute per milligram (the active benzoic acid has identically the same physical–chemical characteristics as the inactive twin, with, of course, the exception of activity).

Now, knowing the total activity added as a "coupling agent" by the preliminary count, and the specific activity of the isolated portion, it becomes a matter of simple ratio to calculate the *weight* of benzoic acid that would, when divided into the total activity, have the same specific activity as the isolate.

Then the subtraction of the small weight of benzoic acid that must necessarily be added to the crude sample as the carrier of the activity, must be made to find the weight of inactive benzoic acid that was in the sample before the activity was added.

AS A TRACER IN BIOLOGICAL RESEARCH

An interesting and easy experiment using carbon

[1] Present address: John T. Ryan Memorial Laboratories, Mine Safety Appliances Company, Pittsburgh.
[2] Recently announced by the Fisher Scientific Company in *Laboratory*, **22**, 154 (1953).

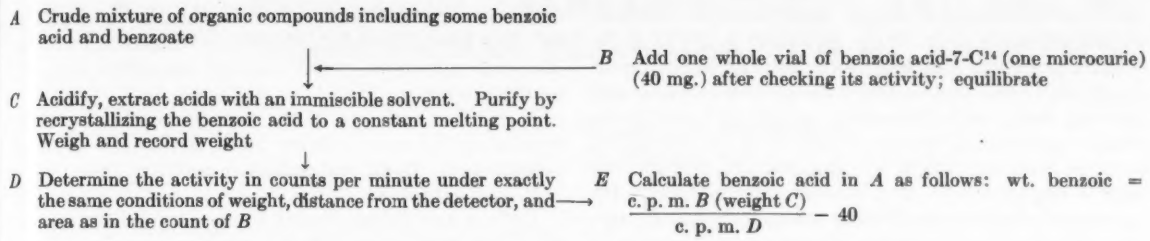
A Crude mixture of organic compounds including some benzoic acid and benzoate
B Add one whole vial of benzoic acid-7-C14 (one microcurie) (40 mg.) after checking its activity; equilibrate
C Acidify, extract acids with an immiscible solvent. Purify by recrystallizing the benzoic acid to a constant melting point. Weigh and record weight
D Determine the activity in counts per minute under exactly the same conditions of weight, distance from the detector, and area as in the count of B
E Calculate benzoic acid in A as follows: wt. benzoic = c. p. m. B (weight C) / c. p. m. D − 40

Figure 1. The Determination of Benzoic Acid in a Complex Mixture by Isotopic Dilution

dioxide-C^{14} to follow the breathing process in living green leaves can be made with a minimum of equipment.

A large green leaf on a living plant is treated and sampled as shown in Figure 2.

The radioactive carbon dioxide is generated right in the Fisher vial from one microcurie of barium carbonate-C^{14} or sodium carbonate-C^{14}, by the addition of a few drops of warm dilute acid.

The leaf's surface is pressed against the mouth of the vial and its natural life processes are allowed to continue, but with the portion encompassed by the vial's mouth breathing a radioactive atmosphere.

At the end of 15 minutes, circles of the leaf tissue can be removed from the body of the leaf with a brass cork-borer of the same diameter as the vial. The first sample should be, of course, the area enclosed by the vial wall, followed by a concentric ring of samples from the immediately surrounding area.

A count of the activity of each circle in the counting apparatus will demonstrate that 96 per cent of the total activity is in the first sample taken, while the sum of the activities from the circles surrounding the first sample will contain the other 4 per cent and will rapidly lose even that small amount.

Repeating the sampling-counting process at much longer intervals of time on samples from the outer edges of the leaf, and from other leaves on the same stem, will demonstrate the speed with which the new, biosynthesized compounds in the leaf are transported to other parts of the plant.

SOLID-LIQUID PHASE EQUILIBRIA

In the study of crystal growth or crystal contamination, and coprecipitation and adsorption phenomena, radioactive tracers can again add useful knowledge unobtainable by other means.

One study, easily made in the school laboratory, is the rate of growth of sucrose crystals in a saturated solution in dilute alcohol.

Figure 2. Where to Remove Samples to Trace the Diffusion of Radioactive CO_2 in a Living Plant

For this particular demonstration, a few hundred ml. of a saturated sugar solution is prepared in water and partially precipitated by the addition of a quantity of alcohol. The suspended crystals are shaken vigorously and allowed to settle.

A 40-mg. quantity of sucrose-C^{14} is dissolved in a few ml. of an alcoholic solution of the same concentration as the supernatant in the larger batch (this involves recording the volumes of water and alcohol used in the preparation of the larger solution). The "active" solution is then added and intimately mixed with the larger solution. An immediate aliquot of a few ml. of the supernatant is taken, completely precipitated with the addition of a small amount of ether, and filtered, and the sucrose crystals are recovered, dried, and counted for activity.

The crystals in the main body of the solution will continue to grow at a slow rate, but in a few days another aliquot can be removed from the supernatant, treated in the manner described, and counted under

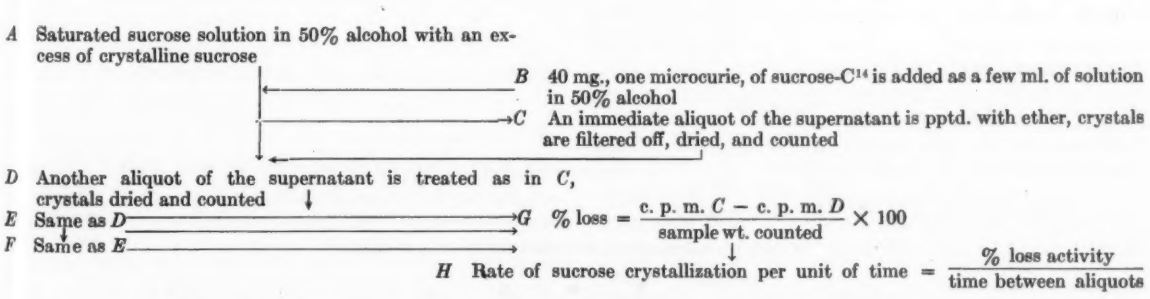
A Saturated sucrose solution in 50% alcohol with an excess of crystalline sucrose
B 40 mg., one microcurie, of sucrose-C14 is added as a few ml. of solution in 50% alcohol
C An immediate aliquot of the supernatant is pptd. with ether, crystals are filtered off, dried, and counted
D Another aliquot of the supernatant is treated as in C, crystals dried and counted
E Same as D
F Same as E
G % loss = c. p. m. C − c. p. m. D / sample wt. counted × 100
H Rate of sucrose crystallization per unit of time = % loss activity / time between aliquots

Figure 3. System for Following Rate of Exchange of Sucrose from the Supernatant to the Crystal Faces in a Saturated Solution

the same conditions of weight, area, and distance from the detector.

After preparing a plot of loss in activity from aliquot to aliquot versus time at which the aliquot is taken, and plotting many such aliquots, a glance will reveal the relative amounts of sucrose deposited on the crystalline surfaces from the radioactive supernatant, and also the rate of deposition for any specific time interval. By varying alcoholic concentration, temperature, and time, the optimum conditions for growing large crystals of sucrose can be established. The general method is diagramed in Figure 3.

LIQUID-LIQUID PHASE EXTRACTION SOLUBILITY

Since many chemical separations involve isolation of the desired material—or removal of an undesired impurity—with an extraction of a solution of the sample with an immiscible solvent, it is often necessary to study the distribution of the chemical compound of interest between the solution liquid and the extracting liquid.

The significant ratios of solute to extracting liquid can be explored by setting them up in the following three-component system and using a radioactive variety of the compound of interest to supply an easy method of measurement. We will base our example on the distribution of benzoic acid between a 50 per cent alcoholic solution and petroleum ether.

To a 25-ml. separatory funnel, add 5 ml. of petroleum ether, 2.5 ml. of anhydrous ethyl alcohol, and 2.5 ml. of water. Twenty mg. of benzoic acid-C^{14} (having an activity of 0.5 microcuries) is added, the funnel is stoppered, and it is shaken vigorously for 30 seconds. The layers are allowed to separate completely.

The bottom phase is the 50 per cent alcohol. It is labeled *A*, and allowed to flow into a separate container. A 2-ml. aliquot is placed in a micro evaporating dish (the tiny metal pans found in some scalers might do—and will save a later transfer). Now 100 mg. of inactive benzoic acid is dissolved in the aliquot and the solution is evaporated to dryness with gentle heating. The dry powder is spread out and smoothed to yield an even deposit.

Now a 2-ml. aliquot of the petroleum ether phase is treated in the same manner, made to dissolve 100 mg. benzoic acid, dried, and spread in another dish. This is labeled sample *B*.

Both of the dishes, *A* and *B*, are counted separately for a determination of their activities by being placed in identical positions in the scaler. Figure 4 shows a plan of the method and the calculation of results.

These simple demonstrations[3] are not just illustrations of useless phenomena. Consider, for example, that the isotopic dilution method of analysis can be a valuable tool to the organic student later on in his advanced experimental work, whether it be method research on new analytical methods or a complicated biochemical investigation.

The researcher into life processes, possibly the medical investigator, can go on from the simple leaf experiment to more complex tracer applications, such as following the metabolism of a new drug or hormone. The study on sucrose crystallization may inspire an embryonic sugar chemist to improve the technology of sugar refining at some future date or—transferring the knowledge gained on sucrose crystals—to invent new and better methods of growing pure sapphire, silicon, or titanium crystals.

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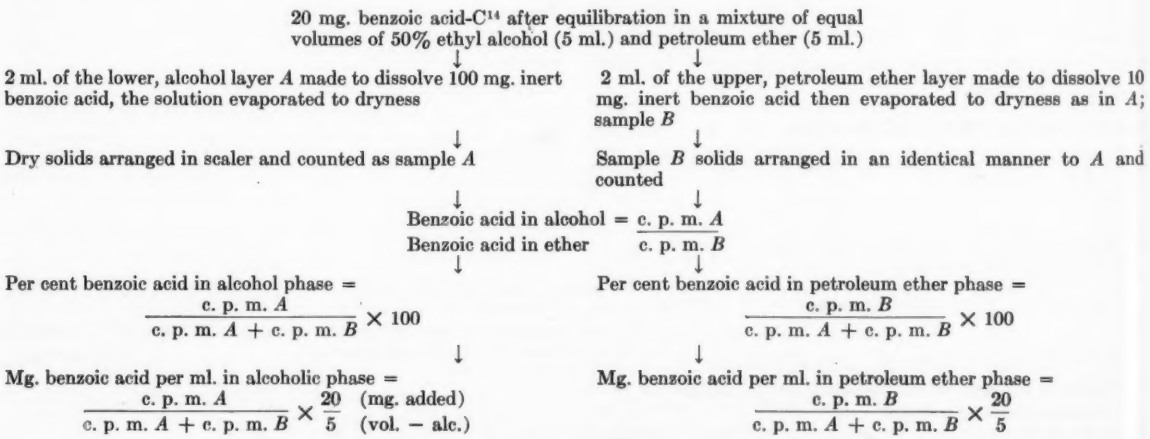
20 mg. benzoic acid-C14 after equilibration in a mixture of equal volumes of 50% ethyl alcohol (5 ml.) and petroleum ether (5 ml.)
2 ml. of the lower, alcohol layer A made to dissolve 100 mg. inert benzoic acid, the solution evaporated to dryness
2 ml. of the upper, petroleum ether layer made to dissolve 10 mg. inert benzoic acid then evaporated to dryness as in A; sample B
Dry solids arranged in scaler and counted as sample A
Sample B solids arranged in an identical manner to A and counted
Benzoic acid in alcohol / Benzoic acid in ether = c. p. m. A / c. p. m. B
Per cent benzoic acid in alcohol phase = c. p. m. A / (c. p. m. A + c. p. m. B) × 100
Per cent benzoic acid in petroleum ether phase = c. p. m. B / (c. p. m. A + c. p. m. B) × 100
Mg. benzoic acid per ml. in alcoholic phase = c. p. m. A / (c. p. m. A + c. p. m. B) × 20/5 (mg. added) (vol. − alc.)
Mg. benzoic acid per ml. in petroleum ether phase = c. p. m. B / (c. p. m. A + c. p. m. B) × 20/5

Figure 4. A Typical Liquid-Liquid Distribution Example

■ ■ ■

BERZELIUS' "JAHRESBERICHT" AND THE INTERNATIONAL ORGANIZATION OF CHEMISTS[1]

WILHELM OSTWALD
(Translated by Ralph E. Oesper)

I RECENTLY had the great pleasure of entertaining at my home a former schoolmate and collaborator with whom, in the long-departed Dorpat days, I had spent many evenings at the beer table discussing scientific matters. Particularly in June, when the winter semester was nearing its close and the northern summer had arrived, with the astounding suddenness which never failed to astonish us, we were prone to sit and argue until the sun reappeared, an event which occurred before the heavens had gotten really dark. The magic of these incredibly short "white nights" frequently affects Central Europeans at their first experience like a volatile inebriating potion. They likewise often have an effect on the natives, and numerous thoughts, which later grew into long chapters or even books, were conceived on such nights.

At first my friend and I explored old memories, at which I was not too good because I had had little time during the intervening years to think of the past. New surroundings and fresh fields of work had more than filled my days and evenings. Collaborators had come from all quarters of the globe and their invitations had later taken me into many countries. Besides, I have never been a "memories" person; I have always lacked time for such mental activities. Consequently, my friend, seeing how things were, asked me to show him my new home which I had designed to fit in with my post—that of a professorial career[2]. He was extremely interested in my library and after looking around he exclaimed: "Heavens! I know that you have always been a little daft about books but I never dreamed that this craze would go to such lengths in your case."

"Yes," I replied, "but this is only partially caused by my own love of books. These days it is simply necessary to have this many books. For the most part, I have these books so that I will not have to read them."

He tapped his head significantly and smiled indulgently. "With you it seems to have started with books and then gone further."

Without realizing it, we had reverted to the argumentative style of the Dorpat days where we had put more emphasis on clarity of thought than on politeness. I shook my head and asked: "What do you do with the books you buy? Do you sit down at once and read them from cover to cover?"

"Of course not," was his reply. "Where would busy men like us get the time to do this ?"

"Well," I said, and in turn pointed to my head.

"We must have facilities for looking things up when the need suddenly arises," he asked, "is that what you mean? Of course, you have to read a borrowed book, at least if you have the intention of returning it. But a book on your own shelf need not be read until such time as you wish to know precisely the thing which was the reason for which you bought the book. I admit you are right."

"Yes, and you are too," I replied, "because in my case it actually has 'gone further.' You know quite well that I have not confined myself to chemistry and that the things which now interest me most are, in general, much more 'paper sciences' than is chemistry."

"But it is certainly no 'paper science,'" he remarked. "Look here my dear friend, at these four thick volumes, which are last year's *Berichte der deutschen chemischen Gesellschaft.* And here are the four volumes of the *Zeitschrift für physikalische Chemie* of the past year. And here, and here, and here—all these are chemical journals for the year 1907. Over there are the thick, closely printed volumes of the *Chemisches Zentralblatt,* which contains the highest concentration obtained by boiling down the chemical work of a single year."

"Yes inde-e-e-d," he replied, trying in vain to stretch out the word to match the length of the rows of books.

Climbing the library ladder and fetching down a thin little volume I said, "Now look at this," handing him the first of a series less than a meter in length. "In this Berzelius published for the year 1820 the first annual report on chemistry. Here in 163 pages, small octavo, he reported on the achievements of the year not only in chemistry but also the related progress in physics, mineralogy, and crystallography, and likewise in geology, assembling the material into extensive, highly readable reports."

"Heavens," remarked my friend, "there has certainly been a tremendous growth since then. Did you say the date was 1820? Just a little less than one hundred years? What if the rate of growth continues at this same pace?"

"Actually, the rate increases steadily," I replied.

"In that case, I am certainly glad that I need not worry about all that." The conversation then turned to other matters.

However, the little Berzelius volume remained on

[1] TRANSLATOR'S NOTE: This essay was composed in 1908. The manuscript was placed at the disposition of the translator by Miss Grete Ostwald, daughter of the author, and curator of the Ostwald Archiv at Grossbothen, Saxony. The text is quite typical of the style and manner of thinking of the great chemical philosopher. It is interesting to compare his proposals with what has transpired in the half century since he wrote these lines.

[2] TRANSLATOR'S NOTE: *Cf.* J. CHEM. EDUC., **25**, 2 (1948).

my desk, and after my friend had left I went to put it into its place. But, as usual, I hesitated a while because I can never resist the tendency to allow such chance occasions to run their course. Nor do I wish to, because such incidents have led me to so many discoveries, which, in seriousness or fun, have proved of great value to me, so that I consider it a technical error to destroy such unbidden possibilities. Furthermore, the factual content of our conversation stayed alive in my mind, namely, the problem of how modern man is going to swim through the sea of paper which threatens to engulf him each day. I had often pondered this predicament.

I remembered that somewhere Wöhler had told that when Berzelius set about putting together his *Jahresbericht* it was his custom to stay away from the laboratory altogether; he surrounded himself with all the books and periodicals which he needed to abstract, and for several weeks he to all intents and purposes withdrew himself from human society and stayed in seclusion until the task was finished. Here again, with a fervor diminished by no amount of labor, this extraordinary man exhibited the unbounded devotion and conscientiousness with which he carried out every project he undertook. For more than a quarter of a century he continued to take on this ever-increasing, strenuous job, and even though he soon excluded physics and geology, this series of annual reports on chemistry (including mineralogy) eventually filled almost a thousand pages. Furthermore, the *Jahresbericht* became the field on which he fought out the conflicts which so embittered and clouded the later years of his life—disputes which filled Wöhler with real distress. Although the name of this faithful student and friend appeared on the title pages of the earlier volumes (the first was translated by Gmelin, who sent Wöhler to study with Berzelius), this was no longer the case from volume 21 (1842) on because Wöhler could not stomach having his name under the same cover with the vitriolic attacks the now aged master made against his (Wöhler's) closest friend Liebig. All that he could do was to blunt the acridity of these utterances as much as possible when he went over the translations prepared by his assistant Wiggers.

However, this is not the place to discuss these painful episodes in the history of chemistry. The details can be found in other of my writings.[3] It is better to examine the beginnings of a process whose usefulness has since made it a vital part of all the sciences. I refer, of course, to the idea of an annual report. I have made no special bibliographic search to discover the name of the inventor of this scientific aid. However, the fact seems to be that for a long period chemistry was the only science which, like a prudent business man, closed the year with an inventory as well as with an accurate balance-sheet. Physics did not follow this lead until a quarter of a century later, *i. e.*, until the young Physikalische Gesellschaft was founded in Berlin and began the publication of its *Fortschritte der Physik*, a most meritorious project, in which, to be sure, there also was evident a strong personal influence, whose effects were distinctly visible in many areas of the later development of this science. The other sciences started their annual reports at much later dates.

None of the sources now available to me reveals who was the first to have the idea of issuing the annual report. However, it probably would be rather easy to glean this information from the minutes of the Swedish Academy around the year 1820. I believe that I am correct in suspecting that it was Berzelius himself. In the introductory remarks to the first volume of his *Jahresbericht* he states: "Since the Academy of Science is today, at the behest of a wise law-giver, giving to the nation an account of the advances made by the sciences in the year just past, not only within its own boundaries but also of those which have come to its knowledge from other countries...."

Obviously, the Swedish Academy planned to publish a general annual account covering all the sciences represented in that body. To what extent this was accomplished beyond the bounds of the physical sciences noted above will be disclosed by examining the records of the Academy. The fact that the other reports, provided they ever saw the light of day, were seemingly very short-lived, and in any event never even approximated the standing immediately attained by the Berzelius *Jahresbericht* and retained through a whole generation, leads me to believe firmly that either Berzelius was the father of the idea or at least was its corporeal uncle. It was only under his diligent, faithful hands that the idea became vitalized and grew to manhood, then made its way around the entire scientific world. After 1847 the Berzelius *Jahresbericht* was taken over by Liebig and Wöhler, but it encountered many difficulties, its health rapidly worsened, and in 1849 (Volume 30) it gave up the ghost.

In our quickly moving times, the space of a year (plus the time necessary to prepare the text, which often was not inconsiderable) is far too long to wait for a report. Consequently, there arose the fashion of putting out reports on individual fields—reports which can be compiled in much less time and which contain references to the allied fields mostly in their annual subject indexes. Such publications proved to be far more viable, and these reports will doubtless serve as the bases of other compilations which will provide a systematic survey for still other appropriate periods, say five or ten years.

Everyone who is active in science in any way whatsoever appreciates the fact that the task of comprehensively organizing a report on various aspects of science is a necessity which constantly grows more urgent. Now more than ever this need presents an international aspect and requires the cooperation of the various countries. Since the needs of the various sciences are dis-

[3] TRANSLATOR'S NOTE: OSTWALD, WI., "Der Werdegang einer Wissenschaft," Leipzig, 1906; see also OSTWALD, WI., "The historical development of general chemistry," a series of lectures delivered at Columbia University in 1906 and published in *The School of Mines Quarterly*, Vol. 27, Nos. 2–4.

tinctly different, it will be best, in the beginning, if each science attempts to set up its own organization. So far as chemistry is concerned, the chemical societies of the various countries are the logical agents since they have proved themselves effective in similar instances. The feasibility of such cooperation is well illustrated by the success of the international commission on atomic weights. To the great benefit of the entire chemical world, this body has capably coped with the important question as to which atomic weights should be accepted. The chemical societies demonstrated that they could function quickly and effectively in bringing this commission into being, and despite some rather hotly debated differences concerning a fundamental point (the numerical unit) scientific discipline proved so potent with respect to the decision of the entire international commission chosen by these societies that (except for two or three recalcitrants, an inescapable characteristic of any general action) there was complete acceptance even by the previous opponents of the majority decision.[4] The extremely gratifying history of this matter provides valuable testimony of how well, even at that time, the technique of international organization for accomplishing scientific objectives was appreciated and with what facility such aims can be attained when this cooperation is used.

Therefore, I now suggest that one of the leading chemical societies (German, American, French, English) invite its sister organizations to send delegates to a preliminary conference to deal with topics of mutual interest. As the first of such subjects to be discussed I propose an agreement on granting members of all these societies the privilege of subscribing to the journals put out by the participating organizations at rates which are not much above the actual cost of production and mailing. It is well known that most of the expense of such periodicals is incurred in the composing room and that the paper and actual printing cost relatively little. Consequently, an increase in the size of the run means little as regards the total cost.

In this way a considerable part of the current literature could be made available, at a comparatively low price, to every member of the cooperating societies. But he will, of course, still be faced by certain difficulties. There is the serious problem of finding time to read the journals. This situation has been recognized by some of the societies who have organized abstract services which have functioned more or less well in solving the difficulty. From the abstracts the chemist can determine what he must or cares to read in the original journal. Obviously, this system represents a tremendous waste of time and work since the same article may be abstracted perhaps a dozen or more times.

Another difficulty is presented by the language handicap. There is no need of repeating here my many discussions of the fact that I see no way out of this impediment except the creation of a synthetic auxiliary language. At present [1908] Esperanto is passing through a crisis which makes it unwise to recommend its adoption; it has not made the requisite progress. On the other hand, I do think that a simplified Esperanto which has been advocated by the international delegation offers distinct advantages over the old Esperanto as a medium for international communication. However, neither of these has as yet developed an artificial chemical language. The creation of such a medium, on the basis of an intensive study of the entire situation, would be another highly fruitful project which might well be sponsored by an international organization of chemical societies. Since chemical nomenclature is already one-half to three-quarters international, it appears entirely feasible to make it a part of all the languages used by chemists. In this event not only the formulas but also the names of substances would be written alike everywhere and perhaps even pronounced alike.

However, I fear that these ideas will be regarded as pure wishful thinking. Consequently, let me return to Berzelius and to what I found in his old *Jahresbericht*. He prefaced the first volume (for the year 1822) with some thoughts on the general conduct of the science—ideas which are strikingly apropos even today. After pointing out that at the time he was writing it was urged by some that science should be regarded as something sacred, to be restricted to the initiates and hence to be protected against profane influences, and that only the results should be communicated to the masses, he continued in a slightly ironical vein:

> This proposition is correct or incorrect according to the different points of view adopted toward the sciences. It is not correct if science is looked upon as a collection of experiences, as a knowledge of phenomena from which one attempts to deduce the causes and from them the laws. Every assemblage of information, no matter how insignificant, becomes intellectual treasure which leads to more enlightened concepts, to clearer views, and to greater applicability. Half-knowledge, scholarly prejudgments among dilettantes formerly constituted scholarship of the highest level; and what is now termed a higher measure of knowledge will, in the course of time, again become only incomplete.
>
> If, however, the sciences are constructed *a priori* from a general fundamental principle, if the speculation, in reverse order, descends from this to experiences, if the audacity of the human power of imagination seeks to take the path of highest understanding, the wax of the Icarian wings will melt in flight, and misconcepts, empty words will then ordinarily take the place of truth and ideas. Considered from this standpoint, the study of the sciences should be reserved to as few as possible, and if at any time this method yields a result which could not be secured by other methods, it will nevertheless always be of the greatest good to humanity if not the speculation but merely the result is made general property.

I trust that this excerpt will induce many readers to take a closer look at the early volumes of the Berzelius *Jahresbericht*. Many more things of interest will be found there.

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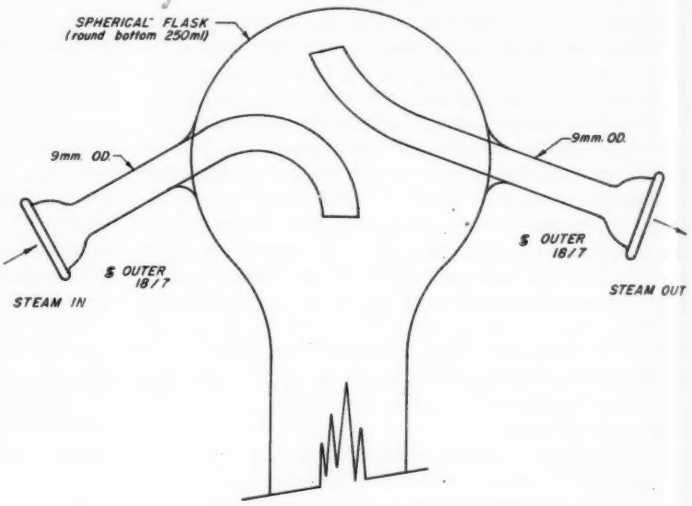
[4] TRANSLATOR'S NOTE: This happy situation was changed materially by World War I. See J. CHEM. EDUC., 17, 562 (1940).

AUTOMATIC SAFETY TRAP FOR LABORATORY STEAM DISTILLATIONS

EDWARD M. HUBBARD
Monsanto Chemical Co., Dayton, Ohio

THE automatic safety trap for laboratory steam distillations described by Nickels[1] has several advantages. Water and oil are removed from the steam and automatically drained, suck-backs caused by decreases in steam pressure are prevented, and excess pressure is released through the water seal.

However, a surge in steam pressure will frequently force all of the water out of the water seal, even when the height of this seal is made twice that previously described. When the water is lost from the seal, steam also escapes and does not pass through the distillation flask. Then water is blown out as rapidly as it condenses and does not accumulate in the seal. A shut-down is then required to add water to the seal. This distinct disadvantage requires considerable attention and time.

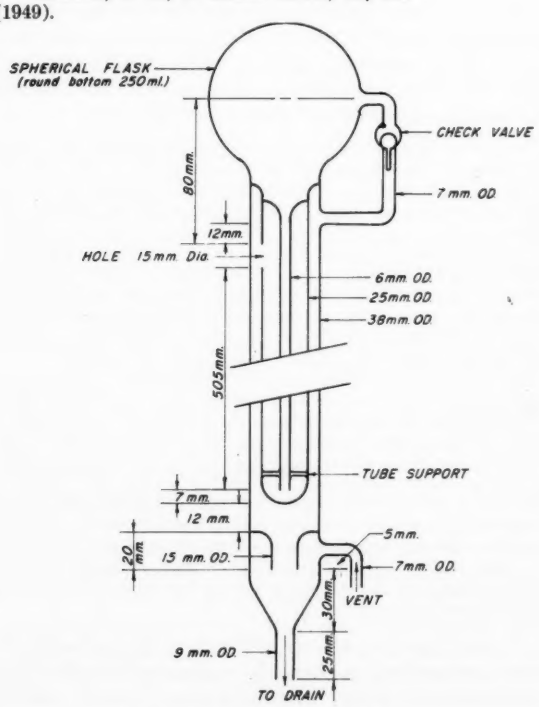


Front View of Head

An automatic safety trap was designed which overcomes this difficulty and has all of the advantages of the Nickels trap. Water, oil, and solids are removed from the steam and led through the water seal to the drain automatically. Suck-backs are prevented by air entering the vent and passing through the check-valve. Excess pressure is released through the water seal. During tests, while steam was admitted through a wide-open valve in the 10 p. s. i. laboratory steam line, the steam exit tube from the trap was suddenly closed. The excess pressure was relieved through the water seal, yet after several minutes the seal still retained the normal amount of water, and the apparatus returned to normal steam delivery immediately when the steam exit tube was reopened.

The trap will supply steam to several steam distillations simultaneously through Y-tubes in the trap exit line. Each distillation can be started or stopped individually without interrupting the others. The height of the water seal can be made in accordance with the load to be carried. Spherical joints are placed on the steam lines to reduce danger of the trap's being broken when rubber tubing is changed. Grease is not needed on the joints.

[1] NICKELS, J. E., J. CHEM. EDUC., **26**, 533 (1949).



Full-length Side View of Safety Trap

COLLIGATIVE PROPERTIES

FRANCIS P. CHINARD
The Johns Hopkins School of Medicine,
Baltimore, Maryland

AN EARLIER note on osmotic pressure[1] was intended to encourage teachers of medical and premedical students to emphasize such fundamental concepts as would obviate or correct misconceptions current in many texts of physiology and of biochemistry. In this note an attempt is made to bring into an integrated system the several colligative properties of importance to physiology and biochemistry. These colligative properties are usually described with emphasis on the experimental methods and on the properties of solutes rather than on the properties of water. A thermodynamic approach is used here; some building of the background is necessary. This might be considered uneconomical were it not for the growing importance of thermodynamic concepts in biochemistry, in physiology, and in certain clinical investigations. A full treatment of the concepts would, however, require more time than could be made available in the conventional medical curriculum. For this reason, development of the background is left to the instructor.

An attempt has been made here, nonetheless, to convey something of the concept of chemical potentials in nonmathematical terms; it is recognized that such a description must be supplemented with further details. There follows the fundamental expression relating changes of chemical potential to changes of pressure, temperature, and chemical composition. From this fundamental expression are deduced, in a manner similar to that used some time ago by Gehlen,[2] the limiting laws of osmotic pressure, of freezing-point depression, of boiling-point elevation, and of vapor-pressure lowering.

THE CONCEPT OF CHEMICAL POTENTIALS

Consider a system comprising several phases with water a constituent of each phase. Each phase can be characterized by its pressure P, its temperature T, its volume V, and its chemical composition (expressed in terms of the mole fractions of the several constituents). Equilibrium with respect to water obtains when there is no mass transfer of water among the several phases. Molecular *exchanges* of water take place in and out of each phase at equal rates though the values of P, T, V, and composition may differ for different phases. With these molecular exchanges taking place at equal rates it may be considered that the average energy available per molecule of water is the same in the different phases. The average energy available per mole of water is the chemical potential, μ, of water. The chemical potential of water is simply the Gibbs free energy of water in a given volume divided by the number of moles of water in the same volume. At equilibrium with respect to water the chemical potentials of water in all the phases are the same. If equilibrium does not obtain with respect to water, there will be mass transfer of water between the phases provided a pathway is available; molecular exchanges occur at unequal rates between the phases; the chemical potentials of water are not equal. The mass transfer occurs from the phase or phases where the average energy or chemical potential of water is higher to the phase or phases where the chemical potential of water is lower. Experimentally, it is found that mass transfer may occur when there are differences between the phases in the values of one of the variables, P, T, or chemical composition. These variables, therefore, determine the relative values of the chemical potential of water in the several phases.

FUNDAMENTAL RELATIONSHIP

The relationship of the variation of the chemical potential of water to variation of pressure, temperature, and chemical composition is given by the following expression[3]:

$$d\mu = \left(\frac{\partial \mu}{\partial P}\right)_{N,f,T} dP + \left(\frac{\partial \mu}{\partial \ln Nf}\right)_{P,T} d \ln Nf + \left(\frac{\partial \mu}{\partial T}\right)_{N,f,P} dT \qquad (1)$$

N is the mole fraction of water, f is the mole fraction activity coefficient; the product Nf is therefore the activity of water; the subscripts to the parentheses indicate that these variables are held constant for the particular variation of μ considered. The relationships which follow:

$$\left(\frac{\partial \mu}{\partial P}\right)_{N,f,T} = \bar{V}; \left(\frac{\partial u}{\partial \ln Nf}\right)_{P,T} = RT; \left(\frac{\partial \mu}{\partial T}\right)_{N,f,P} = -\bar{s}$$

are now substituted in equation (1) to give:

$$d\mu = \bar{V}dP + RTd \ln Nf - \bar{s}dT \qquad (2)$$

$\bar{V}$ is the partial molal volume of water (assumed to be

[1] CHINARD, F. P., J. CHEM. EDUC. **31**, 66 (1954).
[2] GEHLEN, H., *Z. Elektrochem.* **48**, 110 (1942).

[3] The second term on the right relates changes of chemical potential to changes of composition and is obtained from the conventional definition of activity in terms of chemical potentials: $\mu_{H_2O} - \mu^\circ_{H_2O} = RT \ln a_{H_2O}$ where $\mu^\circ_{H_2O}$ is the chemical potential in a standard state in which the activity of water, a_{H_2O}, is unity. Instead of this second term, Gehlen considers the variation of chemical potential with mole fraction and thus limits the applicability of his fundamental relationship to ideal dilute solutions.

independent of pressure in liquid water), R is the gas constant, and $\bar{s}$ is the partial molal entropy of water.

For sufficiently small variations and for systems of two condensed phases or two gaseous phases, the difference of the chemical potentials of water in the two phases may be written (from equation (2)) as:

$$\mu'' - \mu' = \bar{V}(P'' - P') + RT \ln N''f''/N'f' - \bar{s}(T'' - T') \quad (3)$$

The single primes are used to refer to variables or properties in a pure-water phase; the double primes are used to refer to variables or properties in a phase containing other substances in addition to water.

OSMOTIC PRESSURE

Consider an isothermal system consisting of two aqueous phases separated by a membrane permeable only to water. In one of the phases a dissolved substance is present in addition to water. Experimentally, it is found that a pressure difference must be imposed across the membrane in order to establish equilibrium with respect to water and to prevent mass transfer of water from the pure-water phase to the phase containing the solute; it is also found that the greater pressure must be applied to the phase containing the solute. At a given pressure difference the chemical potentials of water in the two compartments are equal; hence, in an isothermal system, equation (3) reduces to:

$$\bar{V}(P'' - P') = -RT \ln N''f''/N'f' \quad (4)$$

On rearrangement, this may be written:

$$P'' - P' = \pi = \frac{RT}{\bar{V}} \ln N'f'/N''f'' \quad (5)$$

where π is the osmotic pressure. The product Nf is the activity; the convention that the activity of pure water in the liquid state is unity is now used. Expression (5) reduces to:

$$\pi = -\frac{RT}{\bar{V}} \ln N''f'' \quad (6)$$

For a sufficiently dilute solution $N''f''$ approaches N'' in numerical value. The mole fraction of the solute is denoted by N_2''. In the present simplified system $N'' + N_2'' = 1$. The product $N''f''$ in (6) may therefore be replaced by $1 - N_2''$. For approximate purposes, $\ln (1 - N_2'')$ may be replaced by $-N_2''$. By definition, $N_2'' = n_2''/(n'' + n_2'')$ where n'' and n_2'' denote the number of moles, in this phase, of water and of the solute respectively. However, because the solution is dilute, n'' is much greater than n_2''. We may then write:

$$\frac{N_2''}{\bar{V}} = \frac{n_2''}{n''} \cdot \frac{1}{\bar{V}}$$

But $n''\bar{V} = V$ where V is the volume of the phase. For n_2''/V we may write C_2'' where C_2'' is the molal concentration of the solute. Expression (6) then becomes:

$$\pi = C_2''RT \quad (7)$$

This is Van't Hoff's limiting law of osmotic pressure.

FREEZING-POINT DEPRESSION

The freezing point of an aqueous solution may be defined as the temperature at which the chemical potential of water in the solution is equal to the chemical potential of pure water as ice at the same temperature. Experimentally, it is found that a pure ice crystal will melt in an aqueous solution held at the freezing point of pure water. There is mass transfer of water from the ice phase to the solution. If the temperature of the solution is gradually lowered there will be found a temperature at which an ice crystal at the same temperature will neither gain nor lose water; there is no mass transfer of water and equilibrium obtains. Below this temperature, there will be mass transfer of water from the solution to the ice phase. There is sought an expression relating the composition of the solution to the difference of the freezing points of the solution and of pure water in a system at uniform pressure.

The difference of the chemical potentials of water in the solution and of pure water at the freezing point of pure water is (from expression (3)):

$$\mu'_{l,T_o} - \mu''_{l,T_o} = RT_o \ln a'_{l,T_o}/a''_{l,T_o} \quad (8)$$

The subscript l denotes water as a liquid; T_o is the freezing point of pure water. Activity is denoted by a. At the freezing point of pure water:

$$\mu'_{l,T_o} = \mu'_{i,T_o} \quad (9)$$

and at the freezing point T'' of the solution:

$$\mu''_{l,T''} = \mu'_{i,T''} \quad (10)$$

The subscript i denotes water as ice. Again from (3):

$$\mu'_{i,T_o} - \mu'_{i,T''} = -\bar{s}_i(T_o - T'') \quad (11)$$

and

$$\mu''_{l,T_o} - \mu''_{l,T''} = -\bar{s}_l(T_o - T'') \quad (12)$$

By subtraction of (12) from (11) there is obtained:

$$\mu'_{i,T_o} - \mu'_{i,T''} - \mu''_{l,T_o} + \mu''_{l,T''} = (\bar{s}_l - \bar{s}_i)(T_o - T'') \quad (13)$$

and by substitution of (8) and (9) in (13):

$$\mu'_{l,T_o} - \mu''_{l,T''} - \mu''_{l,T_o} + \mu''_{l,T''} = (\bar{s}_l - \bar{s}_i)(T_o - T'') \quad (14)$$

From this there is obtained:

$$\mu'_{l,T_o} - \mu''_{l,T_o} = (\bar{s}_l - \bar{s}_i)(T_o - T'') \quad (15)$$

$(\bar{s}_l - \bar{s}_i)$ is equal to L_f/T_o where L_f is the latent heat of fusion. $(\bar{s}_l - \bar{s}_i)T_o$ is the latent heat of transition of water to ice at T_o. By appropriate substitution there is obtained:

$$RT_o \ln a'_{l,T_o}/a''_{l,T_o} = \frac{L_f}{T_o}(T_o - T'') \quad (16)$$

By definition, $a'_{l,T_o} = 1$; $T_o - T''$ is ΔT, the freezing-point lowering. Expression (16) then becomes:

$$-\ln a''_{l,T_o} = \frac{L_f}{RT_o^2} \cdot \Delta T$$

By simplifications similar to those used for osmotic pressure there is obtained:

$$\Delta T = \frac{RT_o^2}{L_f} \cdot C_2'' \tag{17}$$

This is the limiting law for freezing-point depression.

BOILING-POINT ELEVATION

Consider a system consisting of an aqueous phase and a gas phase and maintained at a constant pressure of one atmosphere. The solute is assumed to have a negligible vapor pressure. The boiling point of the solution may be defined as that temperature to which the solution must be raised so that the chemical potentials of water in the solution and in the gas phase be equal when water is the sole constituent of the gas phase (*i. e.*, when the vapor pressure is equal to the total pressure of one atmosphere). At this temperature, there will be no mass transfer of water from one phase to another; if the temperature of the system is lowered, there will be mass transfer of water from the gas phase to the solution. There is sought an expression relating the composition of the solution to the difference of the boiling points of the solution and of pure water when at the same total pressure. The derivation is similar to that for freezing-point depression except that here we deal with $\bar{s}_g - \bar{s}_l = L_e/T_b$. The subscript g denotes the gas phase, L_e is the latent heat of evaporation of water, and T_b is the boiling point of pure water. There is obtained the expression:

$$\Delta T = \frac{RT_b^2}{L_e} \cdot C_2'' \tag{18}$$

This is the limiting law of boiling-point elevation.

VAPOR-PRESSURE LOWERING

Consider two systems each of which consists of an aqueous phase and a gas phase. In the first system, water is considered to be the only constituent of the aqueous phase; in the second system, one or more nonvolatile solutes are present. The total pressures and the temperatures of the two systems are equal. Experimentally, it is found that the amount of water per unit volume of gas phase (and the mole fraction of water in the gas phase) in each system is constant. In each system molecular exchanges take place at such rates in and out of each phase that there is no mass transfer of water. Equilibrium with respect to water obtains in each system between aqueous and gas phases; in each system the chemical potentials of water in the aqueous and gas phases are equal. It is also found, however, that the amount of water per unit volume of gas phase is greater in the first system than in the second system. If the two systems are allowed to communicate through their gas phases, it will be found that mass transfer of water occurs from the first system to the second system. Equilibrium with respect to water does not obtain between the two phases; the chemical potential of water in the first system is greater than the chemical potential of water in the second system. As a matter of convenience and convention, the amounts of water per unit volume of gas phase will be considered indirectly in terms of partial pressures or vapor pressures.

We wish to determine first the difference of the vapor pressures of water in the two systems and to relate this difference to the concentration of solute in the aqueous phase of the second system when the total pressures and temperatures of the two systems are equal. Equilibrium exists with respect to water between the aqueous and gas phases in each system but not between the two systems. From (3) for equal total pressures, the difference of the chemical potentials in the aqueous phases is given by:

$$\mu_l'' - \mu_l' = RT \ln a_l''/a_l' \tag{19}$$

The difference of the chemical potentials of water in the gas phases is:

$$\mu_g'' - \mu_g' = RT \ln a_g''/a_g' \tag{20}$$

Since $\mu_g'' = \mu_l''$ and $\mu_g' = \mu_l'$ we must have:

$$\mu_g'' - \mu_g' = \mu_l'' - \mu_l' \tag{21}$$

If the water in the gas phase behaves as an ideal gas we may substitute p''/p' for a_g''/a_g' where p is the vapor pressure of water. On making this substitution and on making obvious simplifications there are obtained the following equalities:

$$p''/p' = a_l''/a_l' = f_l''N_l''/f_l'N_l' \tag{22}$$

f denotes the mole fraction activity coefficient. Assume $f_l'' = f_l'$. By definition, $N_l' = 1$. Accordingly, we have:

$$p''/p' = N_l'' \tag{23}$$

From this there is obtained:

$$\frac{p' - p''}{p'} = 1 - N_l'' = N_2'' \tag{24}$$

where N_2'' is the mole fraction of solute. Finally there is obtained:

$$p' - p'' = p'N_2'' \tag{25}$$

This relationship indicates that the lowering of the vapor pressure of water in a solution is proportional to the mole fraction of the solute. This is Raoult's law, the limiting law of vapor-pressure lowering.

We wish now to determine the effect of differences of total pressure on the vapor pressure; we wish also to determine the difference of total pressure that must be imposed in order that equilibrium obtain with respect to water between the two systems. In the individual systems we have:

$$\mu_g'' = \mu_l''; \qquad \mu_g' = \mu_l' \tag{26}$$

and

$$a_g'' = a_l''; \qquad a_g' = a_l' \tag{27}$$

On taking the appropriate ratios there is obtained:

$$a_g''/a_g' = a_l''/a_l' \tag{28}$$

If the water vapor behaves as an ideal gas, we may write:

$$p''/p' = a_1''/a_1' \quad (29)$$

In order to establish equilibrium with respect to water between the liquid phases we must have a pressure difference between the liquid phases. Accordingly, for μ_1'' to be equal to μ_1' we must have, from (3):

$$RT \ln a_1''/a_1' = -\bar{V}(P'' - P') \quad (30)$$

By appropriate substitution and rearrangement there is obtained the relationship:

$$RT \ln p'/p'' = \bar{V}(P'' - P') \quad (31)$$

If p'' is less than p', then the total pressure on the solution must be greater than the pressure on the pure water. This pressure difference is exactly equal to the osmotic pressure though there is no membrane involved here.

DISCUSSION

The deduction of the limiting laws from a single fundamental expression serves to point up the interrelationships of these several colligative properties and of the limiting laws. The properties of water are emphasized rather than the solutes; attention is focused on the chemical potentials of water and not on the concentration of the solutes. This is in contrast to current trends in some of the physiological literature where, for example, "osmolar concentrations," "osmols," and even "renal osmolar clearances" are considered.

Water is the major constituent of most biological systems. Changes, of physiological and clinical significance, in the distribution of water among the several body compartments occur because of differences of the chemical potentials of water. The changes in distribution of water are determined in part by differences in the concentrations of other constituents of the compartments, but only in so far as the concentration differences mediate differences in the chemical potentials of water.

ACKNOWLEDGMENT

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SEPARATION AND DETECTION OF THE ALUMINUM ION IN QUALITATIVE ANALYSIS[1]

STERLING B. SMITH and JOHN M. SHUTE
Trinity College, Hartford, Connecticut

THE use of "aluminon," the ammonium salt of aurin tricarboxylic acid, as a reagent in the qualitative test for aluminum is widespread. The purpose of this reagent is to distinguish between the gelatinous precipitate of aluminum hydroxide and a similar precipitate of hydrated silica. When a few drops of the "aluminon" reagent are added to an acidic solution containing the aluminum ion, and the mixture made alkaline with ammonium hydroxide, a red "lake" results.[2] No such color is formed with hydrated silica.

For the past 16 years we have been using in our courses in qualitative analysis in this laboratory the excellent textbook by Hogness and Johnson,[3] now in its fourth edition. Their confirmatory test for the aluminum ion is to dissolve the gelatinous precipitate suspected to be aluminum hydroxide in one milliliter of 3 *M* hydrochloric acid, washing the filter paper with one milliliter of water. Three drops of 3 *M* ammonium acetate and an equal quantity of a 0.1 per cent "aluminon" solution are then added. The solution is stirred, made slightly alkaline with 6 *M* ammonium hydroxide, and gently heated. A red flocculent precipitate indicates the presence of aluminum in the original solution.[4]

The results using these directions have been most unreliable and unsatisfactory. Almost without fail if either iron or chromium ions, especially the latter, are present a false positive test for the aluminum ion is obtained.

This immediately suggests that the previous separation of aluminum from chromium and iron is not complete. A study of this separation and the subsequent test for the aluminum ion was therefore undertaken.

[1] The material for this paper was taken from a thesis by John M. Shute, presented to the graduate committee of Trinity College in partial fulfillment of the requirements for the M.S. degree.

[2] HAMMETT, L. P., AND C. T. SOTTERY, *J. Am. Chem. Soc.*, **47**, 142–3 (1925).

[3] HOGNESS AND JOHNSON, "Qualitative Analysis and Chemical Equilibrium," Henry Holt and Co., New York.

[4] HOGNESS AND JOHNSON, *ibid.*, 3rd ed., **1947**, pp. 397–9.

Preliminary to this study, a sample of aurin tricarboxylic acid was synthesized. This material and five different commercial samples were used in carrying out the "aluminon" test to determine if the unreliability of the test might be due to any variance in the reagent itself. No significant differences were observed.

A thorough study was made to determine the optimum conditions for the red lake formation between "aluminon" and aluminum ions. It was concluded that the best red lake is formed when an acidic solution of pH less than 3.5, containing both the dye and aluminum ions, is reduced in acidity to pH from 5 to 7.2.

A study was made to determine which of the common metals react with "aluminon" to form colored lakes, and the minimum amount of each metal necessary for precipitation was established. Of these metals, lead, zinc, cobalt, manganese, iron, and chromium gave tests similar to that of aluminum. These elements must therefore either be absent or rendered harmless before a solution is tested for aluminum.

By increasing the amount of ammonium acetate from three drops, as directed by Hogness and Johnson, to one milliliter, it was found that zinc, cobalt, and manganese caused no interference unless the amounts present exceeded one millimole. Such amounts are unlikely to be present when the "aluminon" test is performed if the previous procedures have been performed carefully.

Small amounts of lead, chromium, and iron still cause interference even after the increase in added ammonium acetate. Lead, however, is extremely unlikely to be present even in small amounts at this point. Small amounts of chromium and iron are likely to be present at this point, and it is to remove these interfering ions that an alternate procedure has been devised.

The procedure in Hogness and Johnson is to treat a mixture of the chlorides of ferric iron, aluminum, and chromium with hydrogen peroxide and excess sodium hydroxide:

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaCl$$

$$AlCl_3 + 4NaOH \rightarrow NaAlO_2 + 3NaCl + 2H_2O$$

$$2CrCl_3 + 10NaOH + 3H_2O_2 \rightarrow 2Na_2CrO_4 + 6NaCl + 8H_2O$$

Thus, insoluble ferric hydroxide is obtained which may be filtered off and its separation effected. The amphoteric elements remain in solution in the excess of strong base and at the same time the chromium is oxidized to the hexavalent state. When this filtrate is acidified, the aluminum returns to its cation state and the chromium remains in the complex anion.

$$NaAlO_2 + 4HCl \rightarrow AlCl_3 + NaCl + 2H_2O$$

$$Na_2CrO_4 + 2HCl \rightarrow H_2CrO_4 + 2NaCl$$

Addition of slight excess of NH_4OH to this solution produces the white gelatinous precipitate of aluminum hydroxide, leaving chromium in solution.

$$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + NH_4Cl$$

$$H_2CrO_4 + 2NH_4OH \rightarrow (NH_4)_2CrO_4 + 2H_2O$$

This is the white precipitate that is tested in order to distinguish aluminum hydroxide from hydrated silica. This is done, as previously described, by dissolving the precipitate in acid and adding "aluminon" reagent and ammonium hydroxide.

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

$$AlCl_3 + \text{"aluminon"} \xrightarrow{NH_4OH} \text{bright red lake}$$

It is apparent from the above that if the chromium were not completely oxidized by the hydrogen peroxide to the hexavalent state, it would revert to the cation upon acidification, interfering with the aluminum test as shown in the following equations:

$$CrCl_3 + 4NaOH \rightarrow NaCrO_2 + 3NaCl + 2H_2O$$

$$NaCrO_2 + 4HCl \rightarrow CrCl_3 + NaCl + 2H_2O$$

$$CrCl_3 + 3NH_4OH \rightarrow Cr(OH)_3 + 3NH_4Cl$$

$$Cr(OH)_3 + 3HCl \rightarrow CrCl_3 + 3H_2O$$

$$CrCl_3 + \text{"aluminon"} \xrightarrow{NH_4OH} \text{bright red lake}$$

In the endeavor to secure complete oxidation of the chromium, excess sodium peroxide was added to the alkaline solution containing iron, aluminum, and chromium. No improvement was noted. According to Mellor[5] if excess peroxide is present, a partial reduction of the chromium is inevitable upon acidification.

Saturated bromine water was substituted as the oxidizing agent. This proved very satisfactory as far as the chromium was concerned, but iron still interfered. Experiments using varying amounts of sodium hydroxide on a very dilute solution containing ferric ions showed that not all the iron was precipitated and that the more sodium hydroxide used, the greater was the amount of unprecipitated iron. According to work recorded in Mellor,[6] G. C. Wittstein believed that excess sodium hydroxide dissolves a minute amount of ferric hydroxide, but L. Schaffner claims that the ferric hydroxide is in colloidal suspension.

Since it is necessary to have excess sodium hydroxide present to dissolve the amphoteric hydroxides, small amounts of iron must necessarily remain in the filtrate containing supposedly only aluminum and chromium. In order to prevent this iron from later precipitation along with the aluminum hydroxide, it seemed desirable to tie up the iron by complex-ion formation.

The common complexing agents, such as oxalate and tartrate, were of no value since they form complexes with aluminum as well as with iron. A search for a chelating agent for iron which did not unite with aluminum led to the use of the monosodium salt of N, N-dihydroxyethyl glycine (sold in solution under the

[5] MELLOR, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., New York, 1922, Vol. 1, p. 944.

[6] MELLOR, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., New York, 1934, Vol. 13, p. 372.

trade name of Versene Fe-3 Specific).[7] Experiments using Versene Fe-3 Specific showed that relatively large amounts of iron are chelated, whereas the amount of chelated aluminum is not appreciable. For effective chelation the pH should be below 12. Heat as well as time adversely affects chelation.

As a result of these experiments, the following procedure is suggested for the separation of aluminum from iron and chromium and the subsequent use of "aluminon" reagent.

PROCEDURE

Dissolve the precipitate containing the hydroxides of ferric iron, aluminum, and chromium by distributing drop by drop one milliliter of 3 *M* hydrochloric acid over the filter paper on which it was collected. Wash the filter paper with one milliliter of water, adding the wash liquid to the filtrate.

$$Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O$$

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

$$Cr(OH)_3 + 3HCl \rightarrow CrCl_3 + 3H_2O$$

To this solution add two milliliters of 6 *M* sodium hydroxide and two milliliters of saturated bromine water. Stir well. Heat in a beaker of boiling water for three to four minutes. Filter the solution, retaining any precipitate for the test for iron.

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaCl$$

$$AlCl_3 + 4NaOH \rightarrow NaAlO_2 + 3NaCl + 2H_2O$$

$$2CrCl_3 + 10NaOH + 3NaOBr \rightarrow 2Na_2CrO_4 + 3NaBr + 6NaCl + 5H_2O$$

Carefully neutralize the filtrate (which must be clear or refiltered until it is so) with 12 *M* hydrochloric acid and add one drop in excess.

$$NaAlO_2 + 4HCl \rightarrow AlCl_3 + NaCl + 2H_2O$$

$$Na_2CrO_4 + 2HCl \rightarrow H_2CrO_4 + 2NaCl$$

Add five drops of Versene Fe-3 Specific (a 10 per cent solution by volume of the commercial solution) and stir thoroughly. Make the solution alkaline with 6 *M* ammonium hydroxide; add two drops in excess, and stir. Filter this solution, retaining the filtrate for the test for chromium.

$$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$$

$$H_2CrO_4 + 2NH_4OH \rightarrow (NH_4)_2CrO_4 + 2H_2O$$

Wash the precipitate on the filter paper with two one-milliliter portions of water, discarding these washings. Dissolve the precipitate on the filter paper with one milliliter of 3 *M* hydrochloric acid and wash the paper with one milliliter of water, adding the washings to the filtrate. To this solution add one milliliter of 3 *M* ammonium acetate and three drops of "aluminon" reagent. Mix thoroughly. Now make the solution slightly alkaline to litmus with 6 *M* ammonium hydroxide. Heat the mixture in a water bath for from two to three minutes. A bright red flocculent precipitate shows the presence of aluminum.

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

$$AlCl_3 + \text{"aluminon"} \xrightarrow{NH_4OH} \text{bright red lake}$$

Experiments were conducted using the above procedure to determine the maximum amounts of iron (alone), chromium (alone), and iron and chromium together which can be present without interfering with the aluminum test. The minimum amount of aluminum which could be detected in their presence following the above procedure was determined. It was shown that the concentration of aluminum ion normally present in an unknown solution for semimicro qualitative analysis far exceeds the minimum amount which can be detected. At the same time the maximum amount of iron and chromium which can be present without interference is considerably greater than that normally present in semimicro work.

The amount of elements present in a solution taken for semimicro analysis is usually 6×10^{-5} moles. This corresponds to three milliliters of a solution which is 0.02 *M* in concentration of each ion present. However, the concentrations may vary from one-fifth to twice this amount and still be properly separated and detected.

During the course of the investigation, 121 separations were satisfactorily made following the above procedure. As a final check, 20 solutions, each three milliliters in volume were prepared, all of which were 0.02 *M* in concentration of iron and chromium and nine of which were also 0.003 *M* in concentration of aluminum. These were given to an analyst who did not know which solutions or how many contained aluminum. Following the above procedure he correctly determined the presence of aluminum in the nine cases and its absence in the eleven.

In conclusion, it may be pointed out that when this procedure was followed by a class of 22 freshmen taking qualitative analysis, only one man reported aluminum to be present when the unknown contained chromium but no aluminum. This suggests that the test showing the presence or absence of aluminum following this procedure may be regarded to be as reliable as the test for other cations.

[7] Manufactured and sold by the Bersworth Chemical Co., Framingham, Mass.

COMMITTEE ON THE TEACHING OF CHEMISTRY

THE newly constituted Committee on the Teaching of Chemistry (of the A. C. S. Division of Chemical Education) held its first meeting in Cincinnati during the spring Meeting of the Society. It established three immediate objectives: (1) establishment of a program of awards for outstanding high-school chemistry teachers; (2) continuation of the Scientific Apparatus Makers Award; and (3) preparation of a statement of objectives of the Division of Chemical Education and of the Committee itself.

MODIFIED RAMSEY-YOUNG APPARATUS FOR MEASURING VAPOR PRESSURES OF LIQUIDS

WALTER H. DUMKE
Colorado School of Mines, Golden, Colorado

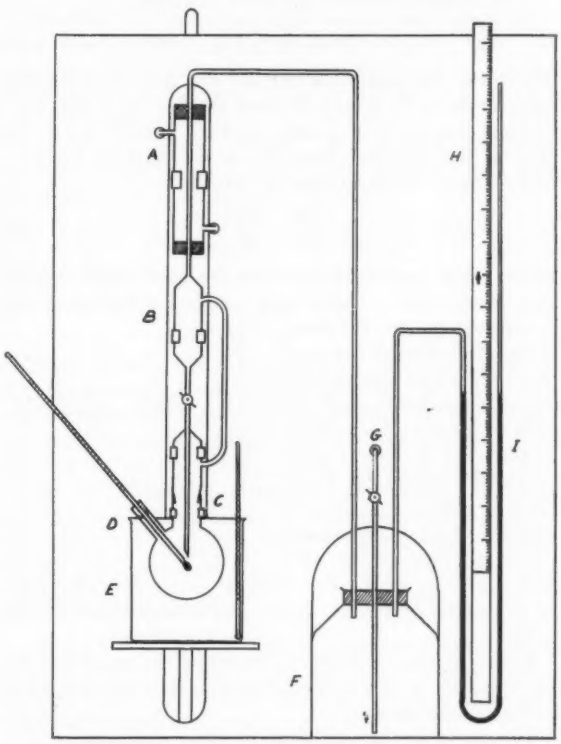
In recent years several modifications of the original Ramsey-Young vapor-pressure apparatus have been devised. The apparatus illustrated is another modification and is used by our students in the physical chemistry laboratory with excellent results.

A very brief description of the apparatus is given. A 500-ml. flask is provided with a ground-glass 35/20 ball joint *C*, a side arm which supports a ground-glass standard-taper 10/30 thermometer, −10°C to 110°C, *D*. An inner-sealed glass tube extends from the reservoir *B* to almost the thermometer bulb which is covered with a wick. A piece of cellophane sponge or glass wool serves well as a hygrometer wick.

The vapors from the flask travel up a side arm and condense in the reservoir *B* with the aid of a cold-water condenser *A*. The system is evacuated through outlet *G* by means of a water aspirator or a Hy-Vac pump. This outlet is connected through a large bottle *F* which in turn connects with an open manometer *I*. An adjustable meter stick *H* slides in a grooved channel. All ground-glass joints are provided with clamps to permit pressure readings from a range of 100 mm. to 800 mm. The entire apparatus is mounted on a portable wooden stand.

In brief, the apparatus is operated in the following manner. The system is evacuated to about 200 mm. pressure, and the water bath *E* is heated to a temperature which will assure that all excess liquid leaves the 500-ml. flask. The flame under the water bath is lowered, the system is further evacuated to about 100 mm., and liquid from the reservoir is slowly allowed to drop on the thermometer wick. When the rate of evaporation becomes equal to the rate of condensation, temperature and pressure readings are made. The pressure within the system is now adjusted to about 200 mm. and again readings are taken. In order to maintain good workable equilibrium conditions, the water bath is kept at a temperature of from 15 to 20 degrees higher than that recorded on the thermometer with the wick.

Many advantages in this design become apparent; however, several should be mentioned. The pressure above the liquid in the reservoir is always equal to the inside system pressure, which permits a uniform flow of drops. A cold-water condenser adds to the convenience of vapor condensation. An adjustable meter stick aids in more accurate pressure readings. The apparatus is leakproof and is mounted on a movable stand which practically eliminates all breakage. Liquids can be added to the reservoir by removal of the 500-ml. flask and application of a slight vacuum.



Our department of physical chemistry has six of these setups which are used by approximately 200 students in any one semester. Each student works independently, which means that each apparatus is used at least 30 times during any semester. Very little breakage was encountered during the five years of student use. On the average, the student found the apparatus easy to manipulate and succeeded in obtaining excellent data.

THE LINE INTEGRAL IN CHEMICAL THERMODYNAMICS

ROBERT M. KALLO
Fresno State College, Fresno, California

STANDARD textbooks on chemical thermodynamics either omit a discussion of the properties of line integrals or only briefly refer to the line integral with regard to its relation to the exact differential. For these reasons it is felt that the following discussion may be of some interest.

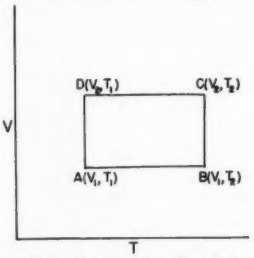
Line integrals frequently have the form:

$$\int_C (M(x, y)\,dx + N(x, y)\,dy) \tag{1}$$

where the integration is carried out over a particular path or curve C, M and N being single valued and continuous functions of x and y for all points of C. In general this integral depends on the path of integration, except for those cases in which:

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \tag{2}$$

where these partial derivatives are also single valued and continuous.[1] Under such conditions the integrand in expression (1) is the exact differential of some function of x and y and the line integral is independent of the path of integration or equal to zero for a closed path provided relation (2) holds for all points in a region within which the closed curve is drawn.[2] In this case the value of the line integral is determined solely by the initial and final coordinates or conditions of the path.



If the partial derivatives expressed in equation (2) are unequal, then the line integral is dependent on the path of integration.

The use of line integrals can be illustrated quite easily when applied to homogenous (simple) systems, uniform in every part with respect to chemical composition and physical condition. Under these conditions the internal energy E of a given system can be taken as a function of any two of the variables P, V, or T.[3] From the first law of thermodynamics, for systems of the type under discussion where the only work done is pressure-volume work,

$$dq = dE + PdV \tag{3}$$

where:

$$dw = PdV \tag{4}$$

q being the heat absorbed by the system, w the work done by the system, P the pressure on the system, and V the volume of the system. Taking E as a function of V and T:

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT \tag{5}$$

Substituting equation (5) in equation (3):

$$dq = \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV + \left(\frac{\partial E}{\partial T}\right)_V dT \tag{6}$$

Applying the reciprocity relation, equation (2), to equation (6),

$$\frac{\partial^2 E}{\partial T \partial V} + \left(\frac{\partial P}{\partial T}\right)_V \neq \frac{\partial^2 E}{\partial T \partial V}$$

Therefore, the line integral whose integrand equals dq is dependent on the path or, the equivalent statement, dq is not an exact differential.

Since the line integral whose integrand is dE does not depend on the path, but that of dq is dependent on the path, then from equation (3) the line integral whose integrand is PdV $(= dw)$ is also dependent on the path.

As a result of the second law of thermodynamics, the quantity dq/T, where dq is the reversible infinitesimal absorption of heat by a system at temperature T, is the exact differential of some function S, the entropy of this system,[4] or:

$$dS = \frac{dq}{T} \tag{7}$$

From equation (6):

$$\frac{dq}{T} = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV + \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT \tag{8}$$

Because of this exactness, the reciprocity relation expressed by equation (2) must hold for the coefficients of dV and dT in equation (8).

The differential of the work content A, defined as $A = E - TS$, is:

$$dA = -SdT - PdV \tag{9}$$

[1] SOKOLNIKOFF, I. S., AND E. S. SOKOLNIKOFF, "Higher Mathematics for Engineers and Physicists," 1941, p. 197.

[2] Strictly speaking, the region must be such that any closed curve drawn in it can be shrunk to a point without crossing its boundary.

[3] EPSTEIN, P. S., "Textbook of Thermodynamics," 1937, pp. 2, 39.

[4] *Ibid.*, p. 58.

Path	w	ΔE	q	ΔS	ΔA
ABC	$RT_2 \ln \frac{V_2}{V_1}$	$C_v(T_2 - T_1)$	$C_v(T_2 - T_1) + RT_2 \ln \frac{V_2}{V_1}$	$C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$	$-C_v \int_{T_1}^{T_2} \ln T dT - S_o(T_2 - T_1) + R(T_1 \ln V_1 - T_2 \ln V_2)$[a]
ADC	$RT_1 \ln \frac{V_2}{V_1}$	$C_v(T_2 - T_1)$	$RT_1 \ln \frac{V_2}{V_1} + C_v(T_2 - T_1)$	$R \ln \frac{V_2}{V_1} + C_v \ln \frac{T_2}{T_1}$	$-C_v \int_{T_1}^{T_2} \ln T dT - S_o(T_2 - T_1) + R(T_1 \ln V_1 - T_2 \ln V_2)$

[a] $\int_{T_1}^{T_2} \ln T dT = T_2 \ln T_2 - T_1 \ln T_1 - (T_2 - T_1)$.

obtained by substituting equations (3) and (7) into the total differential of A. Since A is defined in terms of E, T, and S, its differential is also exact, and the line integral whose integrand is dA is independent of the path, as shown below for the two particular reversible paths illustrated in the figure. Perhaps it should be stated here that only reversible paths are capable of representation by a coordinate system of the type shown in the figure. However, for any variable whose line integral is independent of the path, the change in this variable is only dependent on the initial and final conditions and is independent of whether the process is carried out reversibly or irreversibly.

As an example of the use of line integrals as applied to the variables w, E, q, S, and A, these values have been compiled in the table for a homogeneous system, consisting of one mole of ideal gas having the initial conditions specified by the coordinates of point A in the figure, then proceeding reversibly by either path ABC or ADC to the final conditions specified by point C.

For an ideal gas $(\partial E)/(\partial V)_T = 0$, and integrating equation (8):

$$S = C_v \ln T + R \ln V + S_o \qquad (10)$$

where $(\partial E)/(\partial T)_V = C_v$, and S_o is a constant of integration.[5]

As a typical calculation, q for path ABC is obtained as follows:

$$qABC = \int_{ABC} (PdV + C_v dT) = \int_{T_1}^{T_2} C_v dT + \int_{V_1}^{V_2} PdV$$
$$= C_v(T_2 - T_1) + RT_2 \ln (V_2/V_1)$$

An infinite number of other reversible paths could have been chosen. Regardless of the path, ΔE, ΔS, and ΔA would have the same values, but q and w would be dependent on the path, as shown above for the two paths selected.

Changes in the heat content, H, and the free energy, F, can be handled in an analogous manner, their line integrals being independent of the path. In the latter case, a constant of integration given by equation (10) will appear. Differences in these latter two variables can also be obtained directly from the table, since:

$$\Delta F = \Delta A + \Delta(PV)$$
$$\Delta H = \Delta E + \Delta(PV)$$

From a pedagogical standpoint, the calculation of ΔA, for example, for several different paths between the same initial and final conditions, with the result that the path is immaterial, provides direct evidence concerning the nature of this variable change.

By the use of line integrals over various paths it can readily and effectively be shown that such variable changes as ΔE, ΔH, ΔS, ΔF, and ΔA are independent of the path and that q and w are path-dependent.

ACKNOWLEDGMENT

The author wishes to thank Professor G. Don Alkire, Fresno State College, and Professor Berni Alder, University of California, Berkeley, for helpful suggestions and comments.

[5] LEWIS, G. N., AND M. RANDALL, "Thermodynamics and the Free Energy of Chemical Substances," 1923, p. 446.

PHILLIPS MEDAL AWARD

A SPECIAL striking of the Francis Clifford Phillips Medal in Chemistry of the University of Pittsburgh was presented to Alexander Silverman last month, as a part of the University's commencement program. It was the fiftieth anniversary of Professor Silverman's advent as a member of the full-time staff of the Chemistry Department, the College, and the Graduate School of the University of Pittsburgh.

Dr. Silverman, an internationally recognized authority on glass, is a member of numerous scientific organizations. He has been a member of the Commission on Inorganic Chemical Nomenclature of the International Union of Pure and Applied Chemistry since 1947. Recently he was asked to serve as chairman of the Commission, in which capacity he will preside at sessions in Switzerland during July.

A longtime contributor to THIS JOURNAL, Dr. Silverman has more than 200 papers to his credit in scientific and technical publications.

Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

OFFICIAL BUSINESS

279th Meeting

The 279th meeting of the New England Association of Chemistry teachers was held at Mitchell College, New London, Connecticut, on Saturday, February 12, 1955. In place of the usual morning session, the members made a tour through the plant of the Charles Pfizer Company in Groton, Connecticut, to become acquainted with the modern facilities used to produce antibiotics on a commercial scale. Because the product is a small fraction of the total volume of broth and growing organisms, the disposal of wastes is a major problem. At present it is less expensive to haul them in barges and dump them into Long Island Sound than to convert them into fertilizer, animal feeds, or other products. Until the commercial utilization of these wastes as by-products has been solved the fish of the Sound will continue to "live high."

The business meeting was held at Mitchell College, followed by luncheon and an afternoon technical session. At the latter, David E. Parker, head of the Chemical and Related Techniques Section, U. S. Naval Underwater Sound Laboratory, New London spoke on "Chemistry in the underwater sound laboratory." This laboratory is concerned with transmission of sound through bodies of water and the development of devices to utilize the sound for sending distress signals, detecting obstructions, locating schools of fish, sonic sounding, and during periods of national emergency locating enemy submarines. The chemistry involved consists mostly of selecting suitable materials from which to construct these devices. Some are expendable, like the "Sonarbuoy," but most of them have to withstand the corroding influence of the sea. For example, the stability of polystyrene resins for coating hydrophones or the use of Fiberglas-epoxy resins become applied chemical problems. Development of barium titanate as a piezoelectric ceramic source of ultrasonic energy and its fabrication into useful transducers has been a major development. Barium titanate is produced by calcining a mixture of barium carbonate and titanium dioxide. It is prepared by ball-milling in some calcium titanate and cobalt dichloride (to control sintering), is centrifugally slip-cast in porous plaster-of-Paris molds, and sintered. After slow cooling in the furnace, it is silvered to make an electrical contact.

At the end of his talk, Mr. Parker played an extraordinary recording of underwater sounds produced by fish, porpoises, whales, ship's propellers, and so on. This created a great deal of discussion.

Business Meeting

At the business meeting, conducted by President John A. Timm, the following were welcomed into membership:

Mrs. Vera Currier Allen, Instructor in Physics and Chemistry, Killingly High School, Killingly, Connecticut.
Lt. (j.g.) J. Michael Bestler, Instructor in Chemistry, U. S. Naval Academy, Annapolis, Maryland.
Brother M. Edward, F.S.C., Assistant Professor of Chemistry, La Salle College, Philadelphia, Pennsylvania.
Brother Thaddeus, C.F.X., Chemistry Teacher, St. John's Preparatory School, Danvers, Massachusetts.
Mrs. C. H. Byrd, Instructor in Chemistry, Physics, and General Science, Waynesboro High School, Waynesboro, Virginia.
Ronald V. DuVall, Assistant in Chemistry, Massachusetts College of Pharmacy, Boston, Massachusetts.
Robert I. Ellin, Chairman, Department of Chemistry, Rhode Island College of Pharmacy, Providence, Rhode Island.
Gordon L. Hiebert, Instructor in Chemistry, Bowdoin College, Brunswick, Maine.
Lester Kieft, Chairman, Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania.
Leonard K. Nash, Associate Professor, Harvard University, Cambridge, Massachusetts.
Arthur E. Rondeau, Instructor in Biology and Chemistry, East Senior High School, Pawtucket, Rhode Island.
Norton M. Weiss, Teaching Fellow, Tufts University, Medford, Massachusetts.
Meldrum B. Winstead, Assistant Professor of Chemistry, Bucknell University, Lewisburg, Pennsylvania.

President Timm announced the appointment of the following Chemical Education Committee for the specific purpose of revising the minimum syllabus for high-school chemistry:

Maurice Whitten, Lewiston High School, Lewiston, Maine.
Sister Ernestine Marine, Monsignor Ryan Memorial High School, Dorchester, Massachusetts.
Anna Jane Harrison, Mount Holyoke College, South Hadley, Massachusetts.
Eleanor Tucker, Abbott Academy, Andover, Massachusetts.
Dorothy W. Gifford, Lincoln School, Providence, Rhode Island, *(Consultant)*.

John A. Timm, Simmons College, Boston, Massachusetts (*Ex officio*).

Report of the 16th Summer Conference Treasurer

Cash on hand, May 1, 1954	$ 500.85
Receipts	
Registrations	
Room and Meals	
Miscellaneous	3522.81
Total	$4023.66
Total disbursements	$3399.54
Checks outstanding, Jan. 1, 1955	6.67
Total	$3406.21
Cash on hand, Jan. 1, 1955	$ 617.45

ALICE HOWE
Registrar-Treasurer
Audited March 24, 1955
S. WALTER HOYT
Auditor

Elizabeth Quinn, President of the Connecticut Science Teachers Association, announced the 1955 Connecticut Conference on the Teaching of Science that was scheduled for April 2, at the Yale Law School, New Haven, Connecticut.

Laurence S. Foster, representing the Chemistry Education Committee, Northeastern Section of the American Chemical Society, spoke for the subcommittee on the awarding of the Lyman Churchill Newell Grants, explained how applications were to be submitted. The Newell Grants of $25 each were established this year by the Northeastern Section to aid five young chemistry teachers in the area of the Northeastern Section to attend the 17th NEACT Summer Conference. These grants commemorate a former chairman of the Northeastern Section who was a distinguished chemist and teacher of chemistry. He was for many years the chairman of the chemistry department, Boston University. From 1898 to 1900 he served as the first president of the New England Association of Chemistry Teachers. These awards were made possible by a bequest to the Northeastern Section by his widow.

President Timm announced that nominations for the Davidson Award would be reviewed by the Executive Committee. This award was made possible by a generous gift by Dr. David L. Davidson, Technical Operations, Inc., and is also designated to help defray expenses of a chemistry teacher at the Summer Conference.

17th Summer Conference, Tufts University, August 15 to 20

Roland M. Whittaker, Queens College, cochairman for program, has supplied a complete list of speakers scheduled to appear at the conference:

August 15

Evening. "K-2, the savage mountain," Robert Bates, Phillips Exeter Academy.

August 16

Morning. "Construction of packing models of crystal structures," Henry E. Wendon, Tufts University.
"The historical approach to chemical concepts," S. Madras, Sir George Williams College, Montreal.
Afternoon. "Food canning and scientific research," C. A. Greenleaf, Research Laboratories, National Canners Association.
Evening. "Non-woven fabrics," Raymond J. Spahr, Non-woven Fabrics Division, Chicopee Manufacturing Co.

August 17

Morning. "The hydrothermal growth of quartz crystals," C. A. Walker, Bell Telephone Laboratories.
"Transitor chemistry," Morgan Sparks, Bell Telephone Laboratories.
Afternoon and Evening. Excursion to the First Iron Works Restoration, Saugus, Massachusetts; Boston Red Sox-New York Yankee baseball game, or summer theater party.

August 18

Morning. "Application of nucleonics," Laurence S. Foster, Ordnance Materials Research Office, Watertown Arsenal.
"Quantitative work in the laboratory of the first course in chemistry," Henry Gabriel, Sienna College.
Afternoon. "Sonochemistry and ultrasonics," George E. Henry, General Engineering Laboratory, General Electric Company.
Evening. "The toxicological phase of legal medicine," Charles J. Umberger, Office of Chief Medical Examiner, City of New York.

August 19

Morning. "The toxic principle of poison ivy and related plants," Charles R. Dawson, Columbia University.
Afternoon. "Chemistry in the battle against tooth decay," Irving Glickman, Tufts Dental School.
Evening. "Two years in India," Ruth Ellis.

August 20

Morning. Close of conference.

The dormitories may be available for a few days both before and after the conference for those from a distance who may wish to explore historical sites in the Boston area. Further information may be obtained from the conference secretary, Robert D. Eddy, Tufts University, Medford 55, Massachusetts.

LEALLYN B. CLAPP
Secretary

NECROLOGY

On April 5, 1955, the New England Association of Chemistry Teachers lost one of its most distinguished members when FRANK M. GREENLAW succumbed to a coronary ailment. Not only had he been a member of NEACT from 1904 until his retirement in 1940, and an honorary member since 1941, but he had held important civic positions in the city of Newport, Rhode Island, to an unusual extent for a secondary-school teacher. In addition to his appointment as Coles professor of natural science and head of the science department of the Rogers High School, he held the record in Newport for the longest period of uncompensated service in the city government. He had been a member of the Board of Health for nearly half a century, and as one of the original members of the Equality Milk Association, he was responsible for the initiation of the pasteurization of the Newport milk supply during World War I, and for the extension of the Newport water system; as chairman of the Newport Sewer Commission, he personally supervised the planning for the new sewage treatment plant now under construction. He worked for the establishment of a waste collection system, commencing in 1907, and personally supervised the recent construction of the city incin-

erator. Under his prodding, dental care of the school children was greatly expanded. He served his fellow teachers vigorously on the retirement fund plan and was a founder of the Public Health Nursing Service. Besides these duties he had time to serve as secretary of the Newport Historical Society.

During World War II, shortly after his retirement, he became a wartime teacher of physics at Brown University, and later was awarded the honorary degree of master of arts in recognition of this service.

He was a graduate of Massachusetts Institute of Technology in the class of 1890 and took advanced work at Columbia University. Before taking up his position in Newport in 1903, which he held so long, he had taught at Roxbury High and English High in Boston, held a two year appointment at M.I.T., and had been on the staff of Berwick Academy, Maine, Classical High in Worcester, and English High in Lynn, Massachusetts. During his long membership in NEACT, he had served the Association on many committees and was a frequent host to meetings held in the Southern Division.

Few secondary-school teachers have had the privilege of serving their communities so effectively and in so many capacities. It is safe to say that if all teachers were as vigorous and constructive in their civic contributions as Frank Greenlaw, we today would have an entirely different situation as regards teacher shortages and low pay schedules. He never hesitated to volunteer to serve his community and was in the foreground in every fight to bring the findings of science, medicine, and engineering to the betterment of Newport, and was highly respected by the citizens. In his death the Association has lost one of its ablest and most loyal members.

● ORGANIC SYNTHESES. COLLECTIVE VOLUME 3

Edited by *E. C. Horning*, Secretary to the Board, National Heart Institute, Bethesda, Maryland. John Wiley & Sons, Inc., New York, 1955. x + 890 pp. 28 figs. 15 × 23 cm. $15.

THIS third and latest collective volume of "Organic Syntheses," in bringing together the contents of volumes 20 to 29 inclusive, also brings the material and organization up to date. Errors found since the original printings in single-volume form have been corrected, and there has been a careful rechecking of calculations. Modifications and improvements in procedures have been incorporated. In the many cases where industrial chemical progress has made the products described in the annual volumes available cheaply, this fact is indicated although full details for preparation are still included. The references have been rechecked and brought up to date. The literature has been reviewed thoroughly through *Chemical Abstracts*, Volume 46, for 1952. To aid in making a complete search of the literature, there has been added as a subtitle to each preparation the *Chemical Abstracts* indexing name for the compound when the name differs from the commonly used name.

In the 34 years of its existence the "Organic Syntheses" series has firmly established itself as the authoritative reference on the preparation of organic chemistry reagents. As long ago as 1932 the advantage of having a large number of preparations in a single volume was recognized, and the need was met with the publication of the first collective volume of 580 pages covering the first nine volumes in the series. The second collective volume of 654 pages, covering Volumes 10 to 19, was issued in 1943. The current third volume is by far the largest to date, with 890 pages. The organization, quality, and appearance are essentially the same as previous annual and collective volumes. However, what appears to be lighter weight cloth binding has now been used. Time will tell if this will wear equally well. There is also a slight change in the appearance of the printed cover which, while equally attractive in itself, does not match the two previous collective volumes of the series. This latest volume retains the five previous indexes: Type of Reaction, Type of Compound, Formula, Illustration, and General, and adds a very useful sixth on Preparation or Purification of Solvents and Reagents. Increased publication costs are reflected in a list price of $15, while the corresponding Volume 2 sold for $6.50 when released in 1943. However, this still represents a substantial saving over the individual volume cost of $3.50.

The editor-in-chief, the editorial and advisory board, as well as the publishers are to be congratulated on continuing one of the most valuable series in the organic chemistry field. Future chemists and additional libraries will not only find it more economical and convenient to purchase the collective volumes, but essential if they desire complete collections, since already six of the first nine annual volumes, eight of the next ten, and three of the 20 to 29 series are already out of print.

R. E. DUNBAR

NORTH DAKOTA STATE COLLEGE
FARGO, NORTH DAKOTA

● ELECTROCHEMICAL CONSTANTS

National Bureau of Standards Circular 524. Edited by *Walter J. Hamer*. U. S. Government Printing Office, Washington, D. C., 1953. iv + 310 pp. Many figs. 15.5 × 23.5 cm. $2.

THIS is a collection of 30 short papers contributed by 42 authors including three from Great Britain, one each from Canada, Belgium, The Netherlands, and Malaya, and three from the Bureau of Standards. The longest of the papers consists of 20 pages; the shortest, a brief abstract, of only two pages. All of them, however, furnish important and interesting results of recent thought and experimental work in physical chemistry.

In his Foreword, Dr. A. V. Astin, Director of the Bureau of Standards, states: "The papers in this volume present some of

the latest results, both experimental and theoretical, in the field of fundamental electrochemistry, from many leading establishments in the United States and abroad. They were initially presented at the Symposium on Electrochemical Constants.... during its Semicentennial in 1951." Dr. Walter J. Hamer of the Bureau of Standards, who was chairman of the symposium, prepared the volume and contributed one of the papers.

It would be quite out of the question to attempt to review individually all of these brief papers by some of the great authorities in the field. Although the reviewer is not in a position to select any of these articles as being more meritorious than others, he feels compelled to admit that by reading certain of them his knowledge of the topics involved became more nearly up to date. The field covered is broad and this is likely also to be the experience of others. He takes it upon himself to express to the Bureau of Standards, to Dr. Hamer, and to the other authors, the gratitude of physical chemists everywhere for bringing together so concisely so much valuable material relating to electrochemical constants.

WILLIAM B. MELDRUM

HAVERFORD COLLEGE
HAVERFORD, PENNSYLVANIA

• THE MICROPHYSICAL WORLD

William Wilson, **Professor Emeritus of Physics, University of London. Philosophical Library, New York, 1954. vii + 216 pp. 30 figs. 3 tables. 11 × 17 cm. $3.75.**

WRITTEN by one of the earliest contributors to quantum mechanics, this book is intended to "serve as an introduction and perhaps as an incitement to the more serious study of physical science." A method of episodic treatment of the development of our concepts of subatomic structure is followed. Many great scientists are mentioned and their contributions most succinctly treated. It is inevitable that such a treatment comes out of date all too quickly, but the present volume suffers from stopping before it reaches some of the most fascinating of recent discoveries. Electrons are left on their elliptical orbits, oxygen molecules are given a double bond, mesons are not brought beyond Yukawa's early suggestion.

Authors of books inciting to serious study must tread the very narrow path between oversimplification and overextension of the reader's capacity. Assuming a reader with the equivalent of a good introduction to physical science, corresponding to a beginning college course, this book is oversimplified. Assuming only a secondary-school background, the book is too succinct and advanced. Much of profit is to be found in it, the presentation is superior, but the tone misses the ideal at which it is aimed.

J. A. CAMPBELL

OBERLIN COLLEGE
OBERLIN, OHIO

• MODERN CHEMICAL DISCOVERIES

Richard Clements, **former Editor of *The Chemical Age*. E. P. Dutton & Co., Inc., New York, 1954. xiii + 290 pp. 60 figs. 15 × 22 cm. $5.**

THIS book attempts to replace Sir William Tilden's "Chemical Discovery and Invention in the Twentieth Century." The author's ambition is to embrace all chemical discovery in the last 50 years.

About one-half of the book features advances in organic chemistry. The development of nuclear energy is described in detail. The first part of the book gives a historical background. This background, plus a nodding acquaintance with elementary chemistry, is ample to enable the lay reader to understand the text.

Readers in the United States will notice the English atmosphere in its pages. Had the book been written on this side of the Atlantic, doubtless more attention would be given to petrochemicals, and to inorganic chemistry including hydrides, carbides, ductile titanium, silicones, and synthetic crystals.

"Modern Chemical Discoveries" is a good reference book of the popular type for the school or college library.

ELBERT C. WEAVER

PHILLIPS ACADEMY
ANDOVER, MASSACHUSETTS

• THE DEVELOPMENT OF THE CONCEPT OF ELECTRIC CHARGE

Duane Roller, **American Association for the Advancement of Science, and *Duane H. D. Roller,* University of Oklahoma. Harvard University Press, Cambridge, Massachusetts, 1954. v + 97 pp. 15.5 × 23 cm. Paper bound. $1.60.**

THIS paper-bound volume is Case 8 in the Harvard Case Histories in Experimental Science. Its subtitle, "Electricity from the Greeks to Coulomb," tells the period covered. The authors stick rather closely to their task of discussing the developments which influenced later thinking and experimenting. In this fairly straight line of growth of electrical concepts we find the names of Gilbert, Cabeo, Hauksbee, Gray, Dufay, Franklin, Priestley, and Coulomb as being particularly prominent. Their contributions are described and evaluated in terms of their lasting significance. The reader's interest is sustained by the use of homely detail, quotations, and original illustrations. At the end of the book there are 65 thought-provoking questions and exercises and a bibliography with 97 entries. There is no index.

As minor adverse criticisms it should be noted that students might be puzzled to find "induction" called "electrification by influence" with no hint that this term is now archaic, and, in the epilogue, the attempt to unite the one- and two-fluid theories is neither convincing nor helpful.

The authors frequently step back from their immediate task and show how it illustrates a more general problem in science. This book is definitely successful and will not only make worthwhile reading for students, but should convey new insight to many teachers.

RICHARD WISTAR

MILLS COLLEGE
OAKLAND, CALIFORNIA

• THE LIPIDS. THEIR CHEMISTRY AND BIOCHEMISTRY. VOLUME II: BIOCHEMISTRY. DIGESTION, ABSORPTION, TRANSPORT AND STORAGE

Harry J. Deuel, Jr., **Dean Graduate School and Professor of Biochemistry, University of Southern California. Interscience Publishers, Inc., New York, 1955. xxvi + 919 pp. 31 figs. Tables. 16 × 23.5 cm. $25.**

THE second volume of Deuel's "Lipids" has finally appeared, four years after the publication of Volume I. It had been anticipated that this second volume, devoted to the biochemistry of the lipids, would complete the work. The author now finds that he needs an additional volume to treat adequately the many biochemical aspects of the lipids. This is not surprising in view of the author's statement that "an attempt has been made to list all the investigators who have contributed to any study, irrespective of whether they were the first to report these findings or among the numerous workers who have confirmed and extended the data." Whether or not this objective has been attained, this volume is indeed a monumental work. It will long serve as a reference source for anyone who wishes to familiarize himself with the experimental work that has been done in

the topics that are included in the book. The scope of the literature reviewed is perhaps best indicated by noting that 48 pages are needed for the author's index, and that the references extend far into the fields of physiology, comparative biochemistry, and clinical medicine.

Three of the seven chapters that make up this volume have to do with the digestion and absorption of fats from the gastrointestinal tract, the digestibility of fats, and the digestion, absorption, and digestibility of lipids other than fats. Blood lipids, the occurrence of lipids in the animal as a whole, and lipid distribution in specific tissues, and their secretions are then considered in detail in the last chapters.

Of outstanding interest is the author's treatment of such subjects as the mechanism of fat absorption from the intestinal tract, the relation of cholesterol and plasma lipoproteins to atherosclerosis, the cause of obesity, the development of fatty livers, and lipotropic agents. Conflicting data and viewpoints are fully presented and the reader thus may become fully informed of the problems involved in these, and other highly controversial areas of lipid metabolism.

F. A. CAJORI

UNIVERSITY OF COLORADO
DENVER, COLORADO

● METHODEN DER ORGANISCHEN CHEMIE. BAND IV, TEIL 2: ALLGEMEINE CHEMISCHE METHODEN

Edited by *Eugen Müller.* Georg Thieme Verlag, Stüttgart, 1955. xxviii + 1004 pp. Figs. and tables. 18 × 26 cm. $36.20.

SAMUEL CLEMENS observed that the youth of his day had degenerated to such a state that they would much prefer to gaze upon a half-naked actress than to behold General Ulysses S. Grant in full dress uniform. To the youth of these days who wish to avoid degeneration, this volume of "Die Methoden der organischen Chemie" offers an appealing alternative. Although it may not be as exhilarating as the first, or as elevating as the second, it contains much practical wisdom for leading a calm, peaceful life, especially if one has to deal with catalysts, pyrochemical reactions, electrochemistry, optical antipodes, or biochemical reactions.

The first section (Henecka, 60 pp.) is an excellent treatment of acid-base catalysts. It considers the various theories and presents many examples of activation of carbon-oxygen, carbon-carbon, and nitrogen-containing bonds, as well as decarboxylation. Section two (G. Hesse, 76 pp.) deals with catalysis involving complex cations and anions. The emphasis is on mechanisms and interpretation of a great variety of organic reactions. The third division (Wimmer, 104 pp.) treats the subject of the preparation of catalyst for heterogeneous catalysis. Much of the information in this part is of industrial importance. A great variety of catalysts is described and specific directions are given for their preparation. Section four (G. Schiller and H. Kröper, 80 pp.) concludes the division on catalysis with a thoroughgoing treatment of the experimental procedures for heterogeneous catalytic reactions. Many of the data are assembled in very useful tabular form under the headings of type reaction, equipment, catalysts, temperature, pressure, time, per cent yield, by-products, and references to the literature.

Part five (H. Koch, 20 pp.) describes the techniques for pyrochemical reactions. Attention is centered on the design of laboratory apparatus involving hot wires, external heaters, molten-metal baths, and the handling of micro quantities of materials.

Section six (F. Müller, 48 pp.) on electrochemical reactions outlines the theoretical background and summarizes the electrochemical changes which occur at the anode and cathode.

The seventh subdivision (Theilacker, 34 pp.) recapitulates the methods of resolution of racemic mixtures by spontaneous crystallization, optically active reagents, formation of molecular compounds with an optically active component, adsorption on optically active substrates, and biological resolutions. A final section deals with asymmetric synthesis.

Section eight (Weygand and H. Simon, 190 pp.) is an excellent treatment of the methods of synthesis of isotopically labeled organic substances. The preparation of about 600 labeled compounds is described and presented in tabular form. The arrangement in the tables is by the conventional method of empirical formulas which makes the search for specific compounds very easy.

Part nine (K. Ziegler, 94 pp.) deals with the synthesis and transformations of large ring systems. This section contains an excellent discussion of the theoretical factors entering into these problems as well as a large number of specific laboratory directions for the synthesis of important type-structures.

Sections ten (B. Helferich, H. Stetter, and J. Krebs, 60 pp.) and eleven (W. Reisner, 16 pp.) review the techniques for carrying out biochemical reactions involving either enzymes or microorganisms. The production of a large number of compounds by fermentations is adequately described, as are certain procedures like oxidation, reduction, formation of glucuronic acids, etc. The last section considers the techniques of preparing pure cultures, media, inoculation, and isolation of the products.

The over-all character of this volume of Houben-Weyl is excellent. It will undoubtedly find a valuable place in the laboratories of serious-minded organic chemists.

GEORGE HOLMES RICHTER

THE RICE INSTITUTE
HOUSTON, TEXAS

● PROGRESS IN STEREOCHEMISTRY. VOLUME 1

Edited by *W. Klyne,* Reader in Biochemistry, University of London. Academic Press, Inc., New York, 1954. x + 378 pp. Figs. and tables. 16 × 52 cm. $8.

THE philosopher Zeno observed that the principal occupational hazard of teachers was the loss of common sense resulting from the long association with boys. The authors of this monograph either disprove this assertion, or they have been associating with very mature minds. They exhibit the eminent good sense of not writing an exhaustive textbook in this broad and difficult field, but recognize that Freudenberg's great work of 1933 provides an adequate background. They have concentrated their efforts, therefore, on those stereochemical problems of concepts which were unknown at the time of Freudenberg's book or which have been developed very largely since that time.

Part one (A. D. Walsh, 33 pp.) is a scholarly treatment of the subject of the shapes of molecules. It deals with the interpretation of the experimental data, and theoretical and empirical generalizations. The significant data on a large number of compounds are conveniently arranged in tabular form for easy reference.

Section two (W. Klyne, 54 pp.) is a thoroughgoing treatment of the conformations of six-membered ring systems. The intricate geometry of a large number of both simple and complex polynuclear molecules is set forth in considerable detail. In addition, there is an ample discussion of the stereochemical factors involved in the chemical reactions of these systems.

In part three (P. B. D. de la Mare, 36 pp.) there is a more extended treatment of the stereochemical factors in reaction mechanisms and kinetics. Subjects such as the stereochemistry of nucleophilic substitution, ester formation and hydrolysis, nucleophilic elimination, addition reactions, and racemization of diphenyl derivatives are adequately described.

Chapter four (E. A. Brande and E. S. Waight, 51 pp.) sets forth the relations between the stereochemistry and spectroscopic properties of organic compounds. Attention is centered around the ultraviolet, visible, and infrared absorption spectra of double bonds, single bonds in conjugated systems, and the conformation of alicyclic rings.

The fifth subdivision (J. A. Mills, 41 pp.) examines the correlation of configurations. Compounds are correlated by chemical reactions that do not involve an asymmetric center, kinetic studies of a displacement at an asymmetric center, physical methods like X-ray and electron diffraction, and enzymatic procedures are described and illustrated.

Section six (L. Hunter, 27 pp.) contains an excellent summary of the stereochemistry of the hydrogen bond or bridge. The problems related to the linearity of this type bond, hindered alcohols and phenols, the relations to geometrical isomerism, strength of acids, and the hydrogen bond as a factor in crystal structure are explored.

Part seven (E. J. Ambrose, 35 pp.) is an account of the stereochemistry of compounds of high molecular weight. A discussion of the general principles and experimental methods is followed by an examination of long-chain hydrocarbons, the structure of proteins, and polymers containing ring structures in the main chain.

Chapter eight (V. P. Whittaker, 37 pp.) is an interesting examination of the problems of the stereospecificity of enzyme reactions. Information relating to glucosidases, oxidases, proteolytic enzymes, cholinesterases, and inhibition by organophosphorus compounds and other substances is reviewed.

The concluding section (R. S. Nyholm, 39 pp.) is entitled "The stereochemistry of complex compounds." Over one-half of this chapter is devoted to the nature of chemical bonds involving *s*, *p*, and *d* orbitals. This information is then related to elements with coordination numbers from two to eight. The final part deals with steric changes during chemical reactions. An appendix by A. MacColl summarizes information on bond lengths, bond angles, and van der Waals' radii of atoms.

In a monograph of 360 pages which endeavors to condense information that is constantly undergoing expansion and revision, the editors must of necessity omit many interesting subjects and compress others within narrow limits. This should not elicit captious and frivolous criticisms if it is managed with skill. It is a pleasure to observe that the discriminating selection of topics of "Progress in Stereochemistry" and the high level of competence in handling the ideas merit the most generous applause.

GEORGE HOLMES RICHTER

THE RICE INSTITUTE
HOUSTON, TEXAS

● CHEMICAL CALCULATIONS

H. V. Anderson, **Professor of Chemistry, Lehigh University. Sixth edition. McGraw-Hill Book Co., Inc., New York, 1955. viii + 305 pp. 11 figs. 20 tables. 15.5 × 23.5 cm. $4.75.**

THIS book, now under the sole authorship of Professor Anderson, is chiefly a revision of the fifth edition which was written by Long and Anderson. The sections on significant figures and exponents have been promoted to Chapter I, a highly commendable procedure. Unfortunately, the good section on logarithms, in the appendix of the fifth edition, has disappeared. The great emphasis on worked, illustrative problems with complete dimensions has been retained. A rough count showed more than 160 problems worked out in detail, some by two and three approaches. In many cases experimental techniques are utilized in the approach to a new type of problem. It is a solid, thorough presentation of the calculations to be faced in a beginning chemistry course. There are nearly 900 problems for the student to work; about half of them have answers.

The very breadth and thoroughness of the coverage produces the biggest objection to the book. The price (a reasonable one in view of the fine job done and the nature of the subject) is high. A text, a lab manual, a supplement of this sort, and the cost of books for the beginning chemistry course approaches $15 and that is too much. Sections in the chapter on density and specific gravity and the material on gas analysis might well have been omitted to help cut the cost. It remains, however, a fine investment for the serious student of beginning chemistry.

On page 270 the last two statements are completely contradictory. The next to the last is wrong and should have been omitted. The teacher will be able to rationalize around it, but the beginning student will be trapped by one of the most obtuse points in ionic equilibrium. On this subject, why "SPC" for $K_{s.p.}$ when $K_{ionization}$ is used when dealing with weak acids?

The reviewer has never obtained an "oxidizer" at a plumbing shop, but many "reducers." The author forgets this "nomenclature" on page 141, and with the rest of his colleagues says "oxidizing agents."

HARRY H. BATEY, JR.

STATE COLLEGE OF WASHINGTON
PULLMAN, WASHINGTON

● TWO EARS OF CORN

Claire Leavitt MacDowell. **The Pequot Press, Stonington, Connecticut, 1954. 242 pp. 14.5 × 21.5 cm. $5.**

THIS is the life story of a "printer's devil" on a country newspaper in the Spoon River Country, Illinois, who became advisor to Wilson, House, and Baruch at the Peace Conference in Paris. It is a fascinating, significant story taken from his diary, notes, and scrapbooks of yesterday's great men and political issues and business policies that throw light on our inherited problems today. Not only was he in the thick of political events but he himself occupied a key position in the development of chemical plant foods in this country and in modern application of fertilizers to increase the American farmer's income and our nation's supply of fibers and food. Putting science to work to save packing-house wastes and putting them in fertilizer practice was his crowning contribution to American industry. And all of this is an amazing revelation of how World War I was won, and how the Peace of Versailles was lost. Mrs. MacDowell's straightforward story of her husband's personality and policies is a valuable contribution to our business and political history. This book will also have value in showing how industries start small and grow; how organizations are formed and welded; how business and personal philosophy are developed; how industrial relations are maintained; and how young men get started by recognizing opportunities and doing something about them.

GRETA OPPE

BALL HIGH SCHOOL
GALVESTON, TEXAS

● FIFTY-FIVE COLORFUL YEARS

Ernest T. Trigg. **The Pequot Press, Stonington, Connecticut, 1954. xvi + 307 pp. 14.5 × 21.5 cm. $5.**

IF YOU read "Two Ears of Corn," the life story of Charles H. MacDowell, then you will want to read "Fifty-five Colorful Years." Like MacDowell in fertilizers, so Trigg's book is the story of the paint industry and a firsthand story of how he, as an office boy, climbed up to become one of our industrial leaders and representatives of business during wartime and reconstruction after World War II. It is a story of leaders and politics; of sacrifices and triumphs; OPA, NRA, and the New Deal. His book is alive with anecdotes of outstanding men of the first half of the twentieth century. This autobiography is a wholesome story of American initiative and enterprise. It is interesting that all royalties forthcoming from this book go to a foundation which seeks to foster research and development in the paint and varnish industry by inducing colleges and scientific institutions to establish courses in these fields, and establishing scholarships to promote the industry in every possible way.

GRETA OPPE

BALL HIGH SCHOOL
GALVESTON, TEXAS

● GRIGNARD REACTIONS OF NONMETALLIC SUBSTANCES

M. S. Kharasch, **Professor of Chemistry, and** ***Otto Reinmuth,*** **Research Associate, University of Chicago. Prentice-Hall, Inc., New York, 1954. xxii + 1384 pp. 87 tables. 16 × 23.5 cm. $15.**

THE initial paragraph of the preface to this excellent book reads as follows: "It is reported that Sir William Osler used to open certain of his lectures to medical classes at The Johns Hopkins with the statement that he who knows syphilis knows medicine, for its symptoms can simulate those of any disease in the catalog. With but little more poetic license than the good doctor permitted himself, it might be said that he who knows and understands the Grignard reactions has a fair grasp of organic chemistry, for most fundamental processes have prototypes or analogs in phenomena observable in Grignard systems."

The first five chapters of this book are: Historical Introduction; The Preparation of Grignard Reagents; Estimation and Detection of Grignard Reagents; Constitution and Dissociation of Grignard Reagents; and Some Radical Reactions of Grignard Reagents.

Chapter 6 is devoted to Reactions of Grignard Reagents with Aldehydes, Ketones, and Ketenes. Then follows a series of chapters concerned with reactions of Grignard reagents with compounds having the widest variety of functional groups. Some other chapters are: Allylic Rearrangements in Grignard Reactions; and The Tschugaeff-Zerewitinoff Method for the Determination of "Active" Hydrogen. The Index of Grignard Reagents extends over 16 pages, and the General Index comprises 22 pages.

This monumental work is one of the most comprehensive volumes in any segment of organic chemistry. It is altogether reasonable to expect that in a first edition of so tremendous an undertaking there would be errors and omissions. However, the errors are, on the whole, neither numerous nor serious, and will undoubtedly be corrected in another printing or edition. The authors elected to choose those references which should be included, and the references not included may not be important.

The work is something more than a mere collection and digest of this vast literature. There will undoubtedly be readers who will not agree with some of the observations and ideas presented by the authors. However, the occasional interpolations and suggestions of the authors have the merit that they enliven the presentation in some places and indicate problems deserving additional study.

The number of classics in organic chemistry is not large. This work has every promise of becoming a classic, and organic chemists are deeply indebted to the authors.

HENRY GILMAN

IOWA STATE COLLEGE
AMES, IOWA

● THE ELEMENTS OF CHROMATOGRAPHY

Trevor Illtyd Williams. **Blackie & Son, Ltd., London, 1954. vii + 90 pp. 36 figs. Tables. 13 × 19 cm. 9/6.**

THIS book is designed by the author as a general survey for university students and research workers, of chromatographic methods in use today. When one realizes that a recent book on paper chromatography is 720 pages long and contains some 3795 references, it must be recognized as an accomplishment that Dr. Williams (Deputy Editor of *Endeavor*) has managed to compress information on most fields of chromatography into 90 pages. Figures and excellent color plates help a great deal.

The first chapter (10 pp.) gives a balanced historical introduction to chromatography, reflecting the scholarly work that Drs. Williams and Weil have done in this area. Adsorption chromatography is given 21 pp.; partition chromatography, including a discussion of the separation of inorganic ions, 18 pp.; ion-exchange chromatography, 7 pp.; three chapters on techniques, 20 pp; and a very general chapter on chromatography in industry, 7 pp. There is a bibliography of 17 reference books and reviews, and a short index.

The book deals with elements of chromatography, and only with some of these. Writing in a straightforward style, the author conveys to the reader that chromatography is a rather simple yet powerful analytical tool. This should encourage many chemists to become acquainted with chromatography. If this book will not carry them very far in the solution of new problems, that is not its purpose (as indicated by its title), and at the end of each chapter there are a few selected references to aid the reader in pursuing that particular subject further. The book is printed on good paper and the color reproductions are very pleasing. They have the great advantage of photographs that, being true to fact, they show that in real chromatography not all zones are straight and sharp, nor all spots on paper clearly separated and well defined. This adds greatly to the pleasure of reading the book, and also to the encouragement it should give to an inexperienced chromatographer.

HAROLD G. CASSIDY

YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

● ELECTROPLATING ENGINEERING HANDBOOK

Edited by ***A. Kenneth Graham*** **and** ***H. L. Pinkerton.*** **Reinhold Publishing Corporation, New York, 1955. xix + 650 pp. Many figs. and tables. 18 × 26 cm. $10.**

ELECTROPLATING in the past has been largely a collection of formulas for plating baths, usually not even arranged by chemical type. Now we have a handbook that presents the engineering aspects of the electroplating industry—probably one of the most widely disseminated chemical industries.

The "Handbook" is divided into two sections; the first is on general processing data (391 pp.), whereas the second contains engineering fundamentals and practice (230 pp.). Useful features are the glossary which defines the terms used in the pages that follow, and the first chapter that tabulates many data of importance in electrochemistry.

Part I, on general processing data, presents methods and equipment used in the plating process: surface preparation and cleaning, processing and operating sequences, plating-bath compositions, analysis of plating baths, plating standards and specifications, and surface protection and finishing. It goes beyond this usual material in containing chapters on water requirements, waste disposal, industrial hygiene and safety, and metallurgy for the electroplater. The short chapter entitled Trouble Shooting is most interesting and could have been extended with benefit to all.

Part II, on engineering fundamentals and practice, deals with plant and production engineering problems, such as plant location and layout, tanks, linings, continuous equipment, automatic equipment, exhaust systems, rectifiers, filtration, maintenance, and the like. Design features, calculation methods, curves, and data are given.

The book has a large page size (like Perry's "Chemical Engineers' Handbook") so that a double-column page permits rapid reading as well as large illustrations. The list of 43 contributors who wrote individual chapters in the areas of their specialties is a "Who's Who" in electroplating.

This handbook becomes the standard reference source to the process and engineering features of electroplating. College courses in electrochemistry should make their students familiar with it. Plant and process design courses should consider the electroplating industry as one of the widespread chemical industries.

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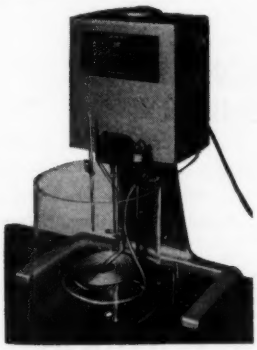
Out of the Editor's Basket

New, Versatile Refrigerated Bath

The new Wilkens-Anderson Refrigerated Bath provides, in one unit, both a conventional water bath and a low temperature bath. It combines the two in one compact unit and the price is little more than that for the single bath.

Temperatures up to 65 deg, C can be provided with a control sensitivity of plus or minus .01 deg. C. By means of an integral mechanical refrigeration system, temperatures down to minus 10 deg. C can also be obtained with the same sensitivity. Pyrex glass jars 12 inches or 16 inches in diameter are available, as well as stainless steel baths.

To increase the versatility even more, a circulating pump can be mounted on the bath housing and cooling or heating medium is pumped to external apparatus such as spectrophotometer, viscosimeters, refractometers, etc.



When frequent changes in bath temperature are to be made, a Rapid-Set thermo-regulator can be ordered with which change in the control point setting of the mercury regulator are made simply and quickly by rotating the cap of the thermoregulator. A complete descriptive bulletin is available from H. J. Wilkens, Wilkens-Anderson Company, 4525 West Division Street, Chicago 51, Illinois.

Molecular Filter

A high-rate Molecular Filter, permitting laboratories to attain filtration of up to 250 ml. per hour, has been introduced by The Emil Greiner Co., 20–26 Moore St., New York 13, New York. This faster filtration rate increases by more than 100 times the rate possible with any comparable type of laboratory filter available.

pH Meter

Line-Operated pH Meter Model 110 incorporates a large-size indicating meter of 7" scale length which covers the entire pH range from 0 to 14 without switching and without reversal of the pointer travel. The instrument can also be furnished in a portable shape with baseboard and carrying cover. The available accessories include a swing-arm adapter for immersing the electrodes by tilting motion and a shielding hood for use of unshielded electrodes. More details are given in Bulletin No. 105 which is available from Photovolt Corporation, 95 Madison Ave., New York 16, New York.

New, Quieter Vacuum Pumps

Here's news that should be music to the tired ears of technicians who are forced to endure the noise and rattle of high vacuum pumps. After five years of research and engineering, Central Scientific Co., 1700 Irving Park Ave., Chicago, Illinois, has developed a new line of mechanical vacuum pumps which operate quietly and with practically no vibration. In fact, the company says, a glass of water placed on top of one of the pumps in operation will hardly show a ripple.

Fluorescent Visual Aid Kit

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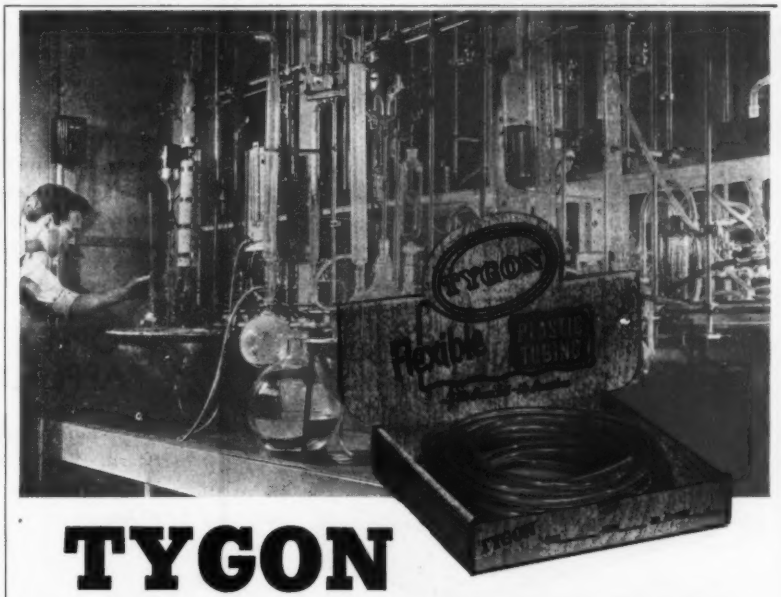

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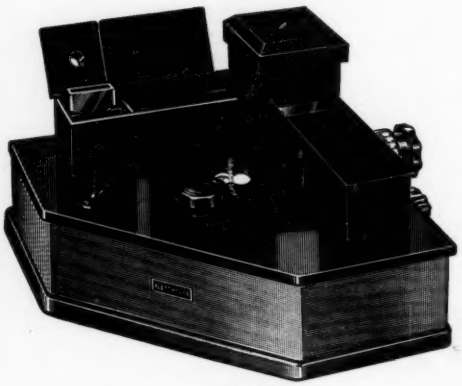

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PROCESS CONTROL SYSTEM DESIGN

By A. J. Young, President of the Society of Instrument Technologists, London. An introduction to the subject of automatic control of industrial processes, beginning with a careful explanation of simple matters and proceeding to more complex aspects. Covers economic considerations, the closed loop, plant characteristics and controllability, time lags, analysis of frequency response, theoretical controllers, continuous control systems, controller settings and quality, components of pneumatic controllers and three-action control, electric and hydraulic controllers, the control loop, transfer stages, and valve characteristics. For chemical engineers, designers of plants and processes, and plant engineers. 320 pages. 5½ by 8 in. Figures and tables. Ready, July. About $7.00.

THORPE'S DICTIONARY OF APPLIED CHEMISTRY

Fourth Edition: Sir Ian Heilbron, Chairman of Editorial Board. Vols. I to X, $20.00 each; Vol. XI, $25.00. Vol. XII, Index. 176 pp. Ready, November. About $7.00.

THE SCIENTIFIC REVOLUTION, 1500–1800

By A. R. Hall, Cambridge University. A "character-study" of the development of scientific ideas and methods, beginning with the state of knowledge at the close of the Middle Ages, and tracing leading issues and significant changes in outlook, the contributions of the philosophers, the impact of new methods of investigation, and the influence of early scientific societies, all leading to the foundations of modern science. 1954. 390 pages 6¼ by 9 in. Frontispiece. $3.75.

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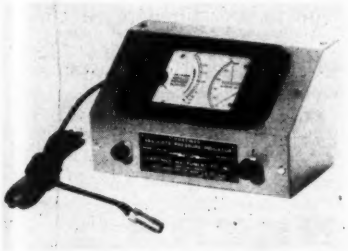
the use of a new fluorescent Visual Aid Kit just put on the market by Ultra-Violet Products, Inc., 5114 Walnut Ave. of San Gabriel, California.

Included in the 68-piece fluorescent Blak-Ray kit are chalks, crayons, tempera colors, colored yarns, assorted cardboards, invisible ink, mechanical pencil with invisible lead, and grease pencils. These visual aids, which markedly increase attention—and retention—also can be purchased individually.

Absolute Pressure Indicator

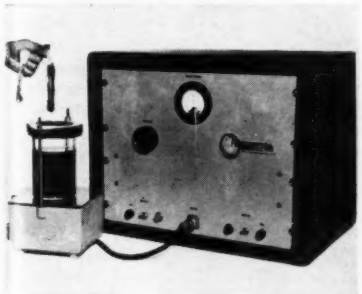
A new Hastings Absolute Pressure Indicator with a range from 0.1 mm. Hg. to 20 mm. Hg and an expanded scale in the 0.5 to 5 mm. range is announced by the Hastings Instrument Co. of Hampton, Virginia.



The new direct reading instrument operates on 115 volts a-c and incorporates the same patented Hastings heated thermopile principle successfully employed in other Hastings vacuum and pressure measuring instruments.

Ultrasonic Generator

Utilizing highly efficient low frequency ultrasonic vibrations, the new Model DR-400 Ultrasonic Generating Equipment announced by Acoustica Associates, Inc., of 420 Seventh Ave., New York, New York, is ideally suited for ultrasonic dyeing and wet-finishing investigation of chemicals or fibers.



Recent work in cellulose, rayon, and other synthetic fibers has indicated far better dyeing results, particularly with such difficult-to-dye materials as Orlon. The time required to achieve level and complete dye penetration and dye bath exhaustion at less than boil temperature was reduced in some cases to $1/6$ that of high-temperature dyeing. The new ultrasonic device might point the way to savings in capital equipment, labor, steam, and chemicals while raising production levels.

Moisture Register

Recent advances in the field of electronics have been incorporated in an improved moisture measurement instrument manufactured by Moisture Register Co., 1510 W. Chestnut St., Alhambra, California, maker of moisture testing equipment.

The improved device, known as the G5 Moisture Register, indicates the per cent of moisture in granular substances, first placing the material under hydraulic compression for uniformity.

Micro-Kjeldahl Apparatus

A Micro-Kjeldahl digestor with individual rheostat controls has been added to the line of laboratory apparatus manufactured by Laboratory Construction Co. of Kansas City, Missouri.

With separate controls that permit variable heat for each of the digestor's six units, laboratory personnel are assured the exact heat they want on all determinations. Address Laboratory Construction Co., 1115 Holmes St., Dept. N, Kansas City, Missouri.

Radiation-shielding Windows

Completely assembled radiation-shielding windows for nuclear research are now available from Corning Glass Works. Consisting of individual castings of radiation-resisting glass up to 10-inches thick stacked together in a frame work, the units are shipped ready to install in test cell walls.

Used to protect research personnel by reducing radiation intensity to a tolerable level, the windows permit direct observation of work carried out remotely in "hot" areas. The new package units, which are available as either wet or dry-type assemblies, eliminate construction and assembly work at the laboratory site.

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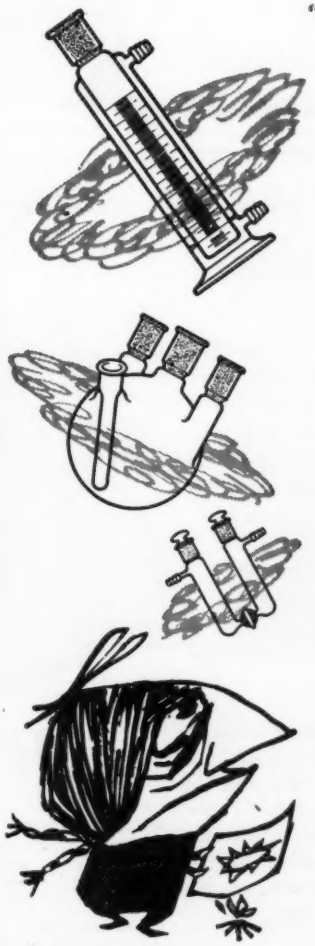

Happy with his last shipment of PYREX peace pipes, this fellow has dreamed up some new uses for special apparatus — and knows where to come for it.

People over in our Special Apparatus Department are used to unusual orders. They don't waste time clucking tongues, because they've seen just about everything. They'll take some tortured memories, give them a few new twists, add a lot of skill and another piece of special apparatus will be on the way. To him, to Mars, or to you.

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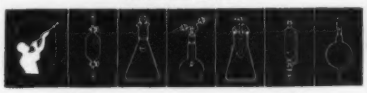

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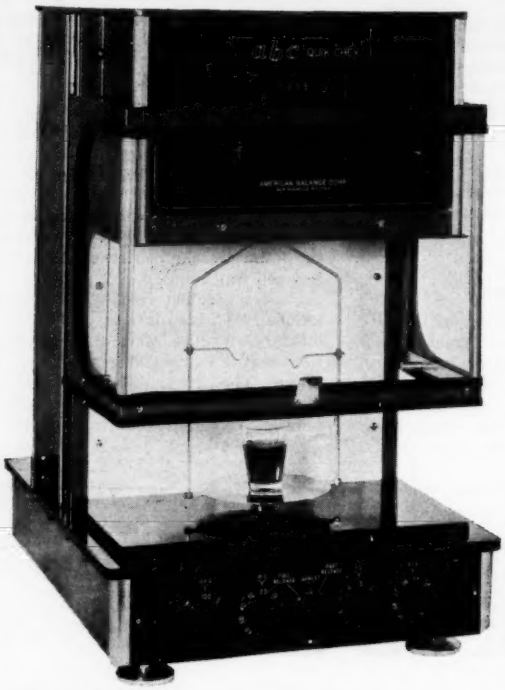

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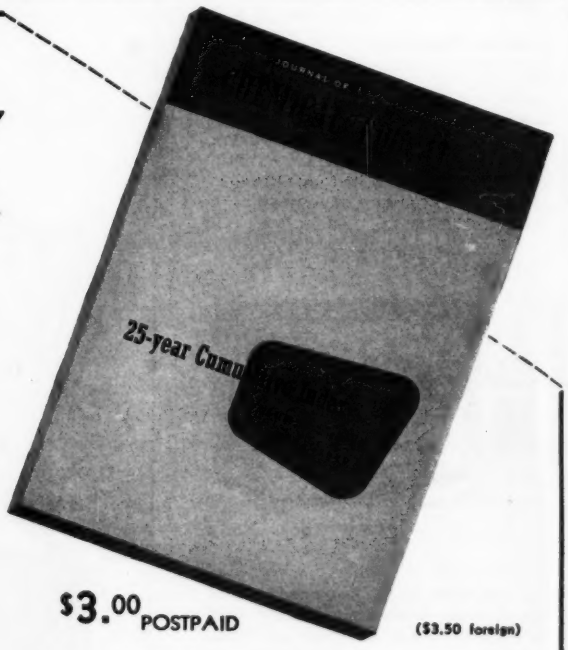
The 25 Year Cumulative Index to the JOURNAL OF CHEMICAL EDUCATION is not a compilation of the annual indexes. It's a completely new index made from a study of each issue published since January 1924. This Cumulative Index is a veritable bibliography of the entire field of chemical education. It's a source book of ideas for the teacher and the chemist in industry alike. If you have access to the JOURNAL, you need a copy of the Cumulative Index. Order it today.



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NEW LITERATURE

● The process industry applications of aluminum for producing everything from beer to bomb shells are thoroughly analyzed in a new 80-page book published by Aluminum Company of America.

The new book, *Process Industries Applications of Alcoa Aluminum*, is available by writing on company letterhead to Aluminum Company of America, 761 Alcoa Building, Pittsburgh 19, Pennsylvania.

● Copies of a new brochure *The Electron Microscope* should prove interesting to any scientific worker. It may be obtained by writing Scientific Instruments, Building 15-1, Engineering Products Division, Radio Corporation of America, Camden, N. J.

● The *L-B Analyzer* is a new quarterly house organ devoted to application of the Infrared Analyzers to industrial and medical problems. If you wish to be placed on their mailing list contact Liston-Becker Instrument Co., Inc., 649 Hope St., Springdale, Connecticut.

● Stock precision-bore glass products in quartz, Vycor and glass with internal diameters controlled to within ±0.0002 inch (for special applications internal diameters may be controlled to within ±0.00005 inch) are illustrated in Fischer & Porter Company's new four-page catalogue No. 80-20. Available on request from Fischer & Porter Co., 379 Jacksonville Rd. Hatboro, Pennsylvania.

● Precision Scientific Co., 3737 W. Cortland St., Chicago 47, Illinois, has published *Bulletin 337*, a 16-page illustrated booklet on uses and technique of "Dry Heat Sterilization." Included in this bulletin is a brief discussion of bacterial resistance to sterilization, a comparison of dry heat sterilization and steam sterilization, the general technique of sterilizing by dry heat and specific procedures for sterilizing such materials as syringes, needles, vaseline and oils, powders and medications.

● Scientific Glass Apparatus Co., Inc., Bloomfield, New Jersey, has just announced the issuance of the 23rd edition of their publication *What's New for the Laboratory*.

Among the many new items featured are four Beckman instruments; silicone rubber-coated Flexible Heating Tape; "Precision" Metabolic Shaking Incubator; Duplex Filamatic; several new glassware items; Wide-Range Zimmerli Gauge; Distilled Water Heater, Bottle Pump; Test Tube Washer; Corning Flared-Top Pipettes; Laboratory Scale; new, improved "Bronwill" Constant Temperature Circulator; plus others.

● Scientific workers will be interested in the availability of a new catalogue illustrating and describing the Hilger X-Ray Diffractometer that is distributed in the U. S. A. by Mr. Richard Ashley, Jarrell-Ash Co., 26 Farwell St., Newtonville, Mass.

● Drage Products, 406 32nd St., Box 330, Union City, New Jersey, offers a publication which gives excellent descriptions and illustrations to explain the basic concept of viscosity and the various types of flow. The variable functions of each type of

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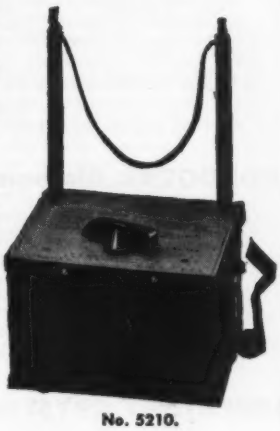
Glass tubing bottles, or jars up to 3 inches in diameter can be cut neatly and quickly with this cutter. Soft glass, Pyrex-brand glass, or other hard-glass tubes can be cut with equal ease. The article is first encircled with a scratch made by a cutter wheel conveniently mounted on the side of the transformer, the scratch is heated by contact with the hot wire, and then cooled quickly by applying water or by blowing on it. No other equipment is required.

The cutting wire is supported on two insulated posts and is heated by current from a 12-volt transformer serving as the base. No. 24 (B & S gauge) nichrome wire is used and is easily replaced. Three extra wires are included. By means of an adjustment on the transformer, the current can be controlled to give the optimum heat for whatever type of glass may be used. An instruction plate is mounted near this control. The unit operates on 115 volts, 50 or 60 cycle A.C. Over-all dimensions are 6 x 4½ x 9 inches high.



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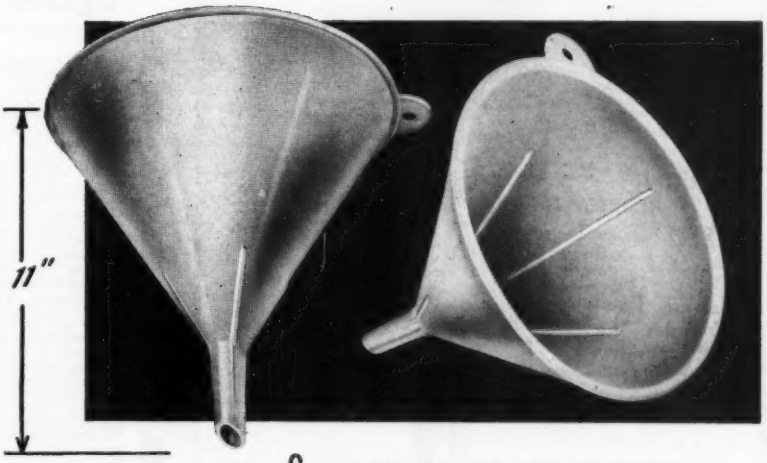

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RESONANCE IN ORGANIC CHEMISTRY

By George Willard Wheland, *University of Chicago.* Based largely on Professor Wheland's *The Theory of Resonance and Its Application to Organic Chemistry*, this new book reflects modern developments and viewpoints. It describes the applications of quantum-mechanical methods to problems of molecular structure. The approach is uniformly chemical and, except for the last chapter, the treatment is qualitative and non-mathematical. An outstanding feature is an appendix on interatomic distances and bond angles—the first serious attempt to list the complete data obtained by all experimental methods for the entire field of organic chemistry. Additional space is given to the molecular-orbital method for treating molecular structure; however, the primary emphasis is still on the resonance concept. Exact terminology is used in all discussions. In the final chapter the author covers the mathematical background and provides the student with a useful introduction to quantum mechanics. *Ready in October. Approx. 830 pages. Prob. $12.00.*

ANDROGENS: Biochemistry, Physiology and Clinical Significance

By Ralph I. Dorfman, *Boston University, and* Reginald A. Shipley, *Western Reserve University.* This is the first book devoted specifically to the broad subject of androgens. Drawing on all the information published in this field over the past thirty years, it discusses both the theoretical and clinical aspects of the male hormones. Included is information on the many uses of androgens in therapy, along with the fundamental research that supports the clinical applications. The structural variations of the steroid molecule are discussed and a structural formula is included for each steroid treated. Also included is a unique compendium of the world's literature on 17-ketosteroids in health and disease. A comprehensive section is devoted to the nomenclature of the steroid hormones. *Ready in November. Approx. 556 pages. Prob. $7.00.*

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flow and the resulting effect upon the final consistency is clearly shown in diagram form.

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● For chemical process industry technicians or research workers who deal with "filtration of any liquid or gas at any temperature" a 16-page catalogue of sintered bronze filters has just been published by the Permanent Filter Corp., 1800 W. Washington Blvd., Los Angeles 7, California. A relatively new filtering medium, sintered bronze is gaining rapid acceptance for applications where ceramic or organic media are not practical because of cost or efficiency in handling corrosives, superheated or extremely cold.

● Arnold O. Beckman, Inc., 1020 Mission St., South Pasadena, California, pioneers of the advanced paramagnetic Oxygen Analyzers that provide a direct measurement of oxygen content, have published an informative new bulletin describing their Model C and Model C2P Oxygen Analyzers.

● A completely new, colorful 16-page catalogue SE 55 on P & H Stainless Steel Equipment for photographic, graphic arts, laboratory, and chemical processing has just been issued by P & H Sales Corp. representing Peck & Harvey Manufacturing Corp., Chicago.

● Three new pieces of literature are available gratis from the Research and Control Instruments Division, North American Philips Co., Inc., 750 S. Fulton Ave., Mount Vernon, New York.

One is a 4-page bulletin titled *Norelco MG 60* which gives design details and application data on a new lightweight portable X-ray unit for radiographic and fluoroscopic work in laboratories and industrial plants. Amply illustrated with photos, the folder covers engineering features of the X-ray control, the X-ray head, and the fluoroscopic stage cabinet.

Twenty Questions and Answers on X-ray Analysis is another clearly explaining the difference in X-ray powder camera, diffractometer and spectrograph equipment and techniques. *Questions and Answers on Magnetic-Particle Testing* is an eight-page booklet which covers procedure and describes problems that can be handled. It also discusses prod and coil techniques, current and voltage conditions, effects of scale, and portable field work.

● The 7th issue of the *Nucleus*, an eight-page two color brochure describes Nuclear's newest radioactivity count rate meter and discusses in detail the principles of radiochromatography. The *Nucleus* is now available on request from Nuclear Instrument and Chemical Corp., 229 W. Erie St., Chicago 10, Illinois.

● A new catalogue is offered by Industrial Instruments, Inc., 89 Commerce Rd., Cedar Grove, New Jersey, on soil moisture

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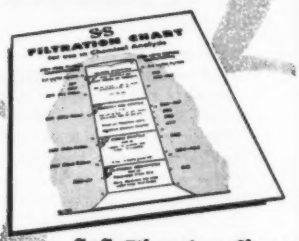

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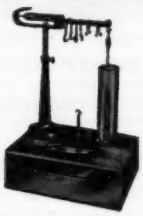

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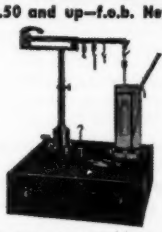

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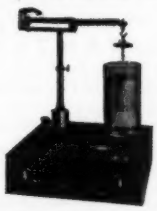

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● The Dajac Laboratories, Chemical Division, The Borden Co., Leominster, Massachusetts, have issued a new catalogue listing over one-hundred reagents for medical research and chemical testing.

● *Selected Laboratory Instruments for Colleges and Universities* is a 17-page catalogue of available apparatus from E. H. Sargent & Co., 4647 W. Foster Ave., Chicago 30, Illinois. Of particular interest are the Thermistor actuated temperature indicating devices.

● General Chemical Division, Allied Chemical & Dye Corp., 40 Rector St., New York 6, New York announces a new catalogue of Baker & Adamson Laboratory Reagents. More than 1000 high purity chemicals are listed as well as information on B & A as to its operations, packaging, etc.

● Ledoux & Co., 359 Alfred Ave., Teaneck, New Jersey, has a new pamphlet on *A Low Cost Instrument for Determining Oxygen in Metal.*

● A new, complete line of highest quality laboratory stirrers is now being offered by Talboys Instrument Corp. of Emerson New Jersey. The line is backed by 19 years' design experience and is called the T-Line of laboratory stirrers. Catalogue sheet and further information available from Talboys Instrument Corp., 13 Ackerman Ave., Emerson, New Jersey.

● An interesting reprint from the November, 1954, *The Lamp*, "Oil and the Atom" is available from the Standard Oil Co. (New Jersey), Room 1626, 30 Rockefeller Plaza, New York 20, New York. It discusses peace-time applications of atomic energy and the effects it will have on living standards. Also consideration is made of the company's experience in nuclear fission.

● Pulp and paper research and development personnel should find a handy guide in Bulletin No. 66, just published by Becco Chemical Division, Food Machinery and Chemical Corp., Buffalo 7, New York, entitled *Becco Laboratory Procedures for Pulp Bleaching*, the new bulletin offers a number of test procedures for preliminary evaluation of various peroxide pulp bleaching treatments.

● A group of four papers discussing orientation and training in modern industry are now available in a publication of the proceedings of the 22nd Annual Meeting of the Engineers' Council for Professional Development, held recently in Cincinnati, Ohio. The publication includes a copy of the brochure describing the program for young graduate engineers during the "First Five Years" and a copy of the brochure reporting on "The Community Project in Professional Development" which has been studied recently in Cincinnati. Copies of the publication are available by addressing ECPD Committee on Professional Training, 322 Baldwin Hall, Cincinnati 21, Ohio.

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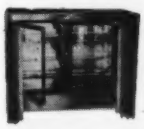

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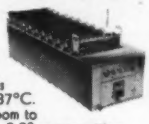

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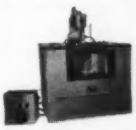

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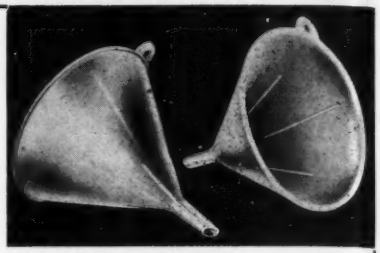

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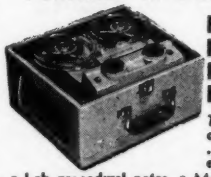

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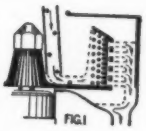
FIG.1

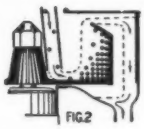
FIG.2

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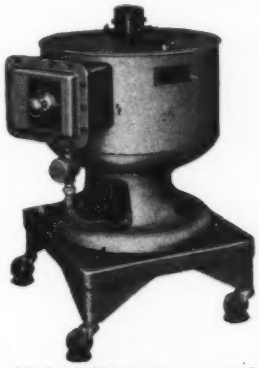
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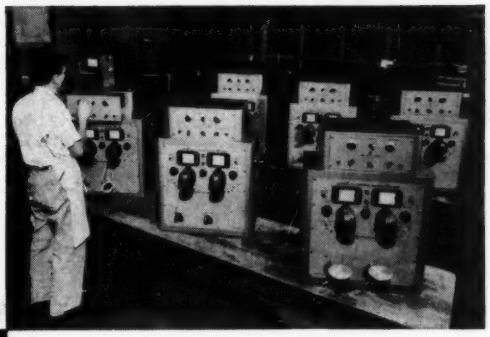

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